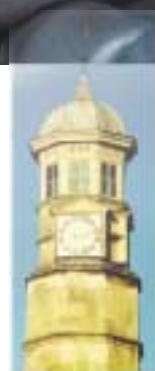


# *The Kinetics and Dynamics of Elementary Gas Phase Reactions, 2002*

*Celebrating the career of  
Professor Ian W.M. Smith F.R.S.*



**THE UNIVERSITY  
OF BIRMINGHAM**

**REPORT DOCUMENTATION PAGE**

Form Approved OMB No. 0704-0188

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<b>1. REPORT DATE (DD-MM-YYYY)</b> 21-10-2002			<b>2. REPORT TYPE</b> Conference Proceedings	<b>3. DATES COVERED (From – To)</b> 16 September 2002 - 18 September 2002	
<b>4. TITLE AND SUBTITLE</b> The Kinetics and Dynamics of Elementary Gas-Phase Reactions			<b>5a. CONTRACT NUMBER</b> F61775-02-WF080		
			<b>5b. GRANT NUMBER</b>		
			<b>5c. PROGRAM ELEMENT NUMBER</b>		
<b>6. AUTHOR(S)</b> Richard P. Tuckett, editor			<b>5d. PROJECT NUMBER</b>		
			<b>5d. TASK NUMBER</b>		
			<b>5e. WORK UNIT NUMBER</b>		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> University of Birmingham Edgbaston Birmingham B15 2TT United Kingdom			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> N/A		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> EOARD PSC 802 BOX 14 FPO 09499-0014			<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>  <b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> CSP 02-5080		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> <p>The Final Book of Abstracts for The Kinetics and Dynamics of Elementary Gas-Phase Reactions, 16 September 2002 - 18 September 2002</p> <p>This is an interdisciplinary conference, given in honor of Prof. I.W.M. Smith. Topics include:          Reaction Dynamics and Energy Transfer; Gas Kinetics and Atmospheric Chemistry; Astrochemistry          Theoretical Chemical Dynamics and Kinetics</p>					
<b>15. SUBJECT TERMS</b> EOARD, Chemistry, Kinetics					
<b>16. SECURITY CLASSIFICATION OF:</b> a. REPORT UNCLAS			<b>17. LIMITATION OF ABSTRACT</b> UL	<b>18. NUMBER OF PAGES</b> 77	<b>19a. NAME OF RESPONSIBLE PERSON</b> Ingrid Wysong
b. ABSTRACT UNCLAS					<b>19b. TELEPHONE NUMBER</b> (Include area code) +44 (0)20 7514 4285

# *The Kinetics and Dynamics of Elementary Gas Phase Reactions*

*Celebrating the career of Professor  
Ian W.M. Smith F.R.S.*

*September 16-18<sup>th</sup> 2002,  
The School of Chemical Sciences,  
University of Birmingham.*

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# Conference Map and Information

## Registration and Accommodation

Conference registration will occur from 11 am on Monday in the Reading Room on the 2<sup>nd</sup> floor of the Haworth building (number 12 on the enclosed map). Shuttle buses will run between the car park to the front of the School of Chemical Sciences and Mason Hall and Lucas House between 11 am and 1 pm. Conference attendees are encouraged to obtain keys for their accommodation during this time or following the final scientific session of the day. Lucas House (map number 67) is within easy walking distance of the School. Mason Hall is approximately 20 minutes walk (map number 74).

## Shuttle Buses

Shuttle buses will run between the School of Chemical Sciences and Lucas House and Mason Hall at the following times.

Monday 16<sup>th</sup>, School to Mason Hall and Lucas House and back: 11 am-12.30 pm.  
Monday 16<sup>th</sup>, School to Mason Hall and Lucas House: 6-6.30 pm.  
Tuesday 17<sup>th</sup>, Mason Hall to School: 8.20 am and 8.40 am.  
Tuesday 17<sup>th</sup>, Lucas House to School: 8.40 am.  
Tuesday 17<sup>th</sup>, School to Mason Hall and Lucas House: 5.15-6.30pm.  
Tuesday 17<sup>th</sup>, Mason Hall and Lucas House to Staff House: 6-6.45pm.  
Wednesday 18<sup>th</sup>, Mason Hall to School: 8.10 am and 8.30 am.  
Wednesday 18<sup>th</sup>, Lucas House to School: 8.30 am.

## Lunch and Coffee

Lunch will be served between the times indicated on the conference programme in the Reading Room on Level 2 of the Haworth building. Following lunch, coffee will be served in the Level 1 / ground floor foyer area, prior to the recommencement of the scientific programme. Morning and afternoon tea/coffee will be provided at the times indicated on the conference programme in the Level 1 / ground floor foyer area.

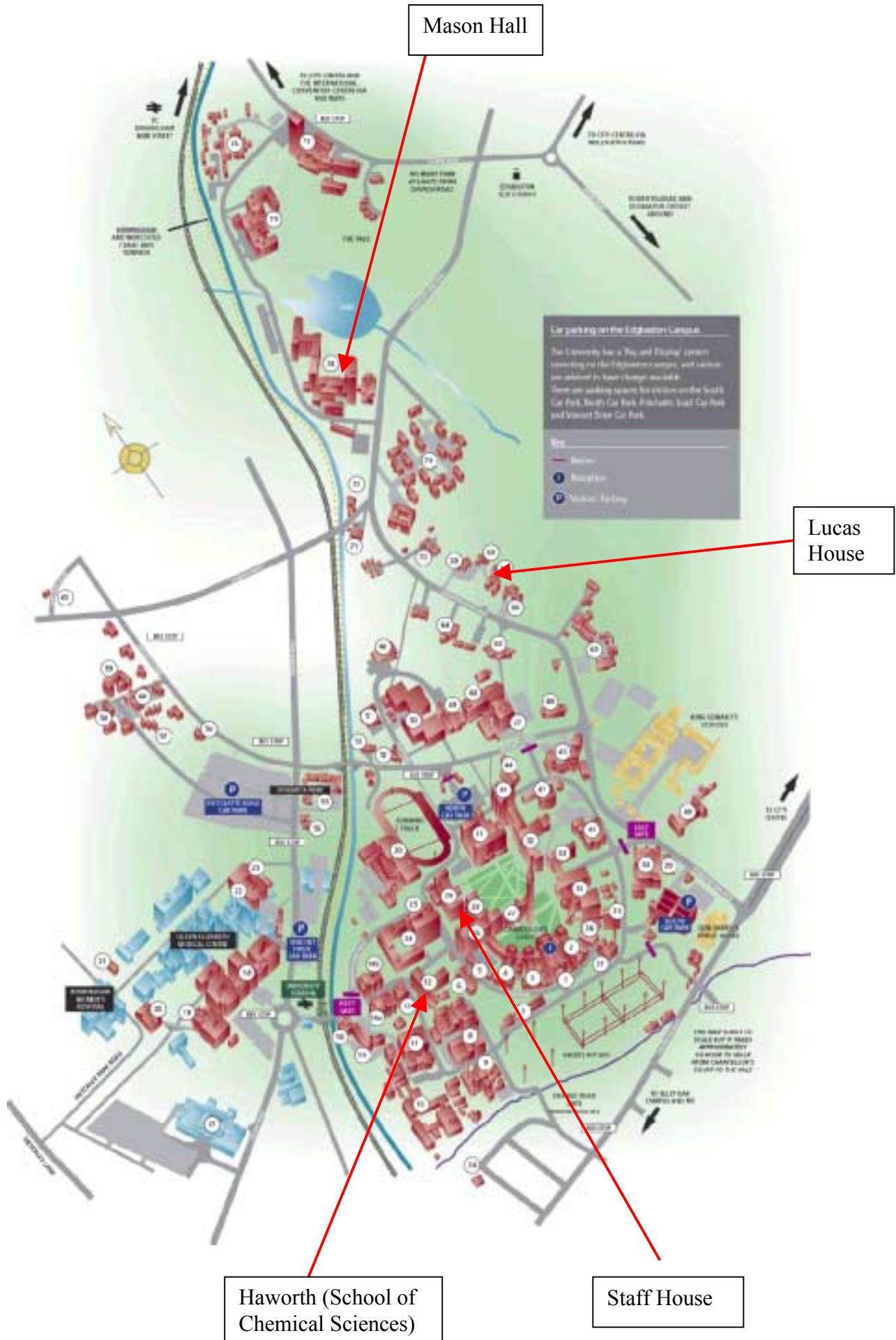
## Poster Session

The poster session will follow dinner on Monday evening. Poster boards will be numbered according to the page numbers of the abstracts. Please find the appropriately numbered poster board for your presentation. Posters should be removed at the end of the session.

## Conference Banquet

The conference banquet will be held in Staff House (map number 28). A drinks reception will begin at 6.30 pm on the 1<sup>st</sup> floor accompanied by musical entertainment. The banquet will begin at approximately 7.45 pm in the Noble Room. Shuttle buses will be available after the event to Mason Hall and Lucas House.

Jonathan Reid Ian Sims Richard Tuckett  
The Organising Committee, 12/9/02



# Conference Programme

## Monday 16<sup>th</sup> September

1100-1230	Registration, School of Chemical Sciences (Reading Room) Minibus shuttle between the School and Mason Hall/Lucas House
1230-1330	Lunch (Reading Room)
1330-1345	Welcome by Conference Organisers (Lecture Theatre 101)

### ***Scientific Session: Gas Kinetics and Atmospheric Chemistry*** ***Chair: Dr Chris Morley, Shell Global Solutions***

1345-1430	Prof A. R. Ravishankara (NOAA, USA) <i>From the Strong to the Weak: OH-Molecule Adducts and Their Impact on Kinetics and the Atmosphere</i>
1430-1515	Dr Mike Frost (Heriot-Watt University, UK) <i>REMPI-LIF Studies of Ion-Molecule Reactions</i>
1515-1545	Tea/Coffee
1545-1630	Prof Dr Reinhard Zellner (University of Essen, Germany) <i>Atmospheric Gas Phase / Particle Interactions : Concepts, Techniques And Results</i>
1630-1715	Prof Gus Hancock (University of Oxford, UK) <i>Time Resolved Infrared Emission: An Academic Comfort Blanket</i>
1715-1800	Prof Mike Pilling (University of Leeds, UK) <i>Radical Kinetics in Combustion and Atmospheric Chemistry</i>
1800-1830	Minibus shuttle service from School of Chemical Sciences to Mason Hall / Lucas House
1830-1930	Dinner (Mason Hall)
2000-2200	Poster Session (Mason Hall)

## **Tuesday 17<sup>th</sup> September**

0700-0815 Breakfast, Mason Hall  
0820, 0840 Minibuses from Mason Hall to School of Chemical Sciences  
0840 Minibus from Lucas House to School of Chemical Sciences

### ***Scientific Session: Astrochemistry***

***Chair: Professor John Maier, University of Basel***

0900-0945 Prof Eric Herbst (Ohio State University, USA)  
*Interstellar and Circumstellar Chemistries: The Role of Neutral-Neutral Reactions*

0945-1030 Dr Ian Sims (University of Birmingham, UK)  
*Low Temperature Molecular Collisions*

1030-1100 Tea/Coffee

1100-1145 Dr Bertrand Rowe (Université de Rennes 1, France)  
*Obtaining Molecular Data for Astrochemistry with the CRESU Technique*

1145-1230 Prof David Field (University of Aarhus, Denmark)  
*Cold Collisions of Electrons and Molecules*

1230-1345 Lunch

### ***Scientific Session: Theoretical Chemical Dynamics and Kinetics***

***Chair: Professor Peter Knowles, University of Birmingham***

1345-1430 Prof W H Miller (University of California-Berkeley, USA)  
*Using Semiclassical Theory to Include Quantum Effects in Classical Molecular Dynamics Simulations*

1430-1515 Prof Millard Alexander (University of Maryland, USA)  
*The Long Saga of the NO Molecule*

1515-1545 Tea/Coffee

1545-1630 Prof David Clary (University College, London, UK)  
*Chemical Reactions at Lower Temperatures: Has Theory Stimulated Experiments?*

1630-1715	Prof Dr Jürgen Troe (University of Göttingen, Germany) <i>Statistical Adiabatic Channel and Classical Trajectory Calculations for Reactions of Astrophysical Importance</i>
1715-1830	Minibus shuttle service from School of Chemical Sciences to Mason Hall / Lucas House
1800-1845	Minibus shuttle service from Mason Hall / Lucas House to Staff House
1830-1945	Reception (1 <sup>st</sup> floor, Staff House)
1945	Conference Banquet (2 <sup>nd</sup> floor, Staff House)

### **Wednesday 18<sup>th</sup> September**

0700-0800	Breakfast, Mason Hall
0810, 0830	Minibuses from Mason Hall to School of Chemical Sciences
0830	Minibus from Lucas House to School of Chemical Sciences
NB Baggage can be left in locked room on level 2 of Haworth building	
<i>Scientific Session: Reaction Dynamics and Energy Transfer</i> <i>Chair: Professor Piero Casavecchia, Università di Perugia</i>	
0845-0930	Prof John Polanyi (University of Toronto, Canada) <i>Reaction Dynamics a Molecule at a Time: Thermal, Photo-induced and Electron-induced Reaction of Adsorbates on Si, by STM</i>
0930-1015	Prof Brad Moore (Ohio State University, USA) <i>Not-So-Statistical Reactions</i>
1015-1045	Tea/Coffee
1045-1130	Prof Fleming Crim (University of Wisconsin-Madison, USA) <i>Bond-Selective Bimolecular Reactions of vibrationally Excited Molecule</i>
1130-1215	Prof Zamik Rosenwaks (Ben Gurion University, Israel) <i>The Chemical-Oxygen Iodine Laser: Exploitation of the Magic Oxygen Singlet Delta Molecule - a Status Report</i>
1215-1300	Prof Curt Wittig (University of Southern California, USA) <i>Local Quantum Chaos in Helium Nanodroplets'</i>
1300-1400	Lunch

## Sponsors

The organising committee gratefully acknowledges the generous sponsorship for this meeting offered by the following commercial and non-commercial organisations:



**European Office of Aerospace Research and Development of the USAF\*\***



**The Royal Society of Chemistry**

- **Angela and Tony Fish Bequest\*\***
- Astrophysical Chemistry Group\*
- Birmingham and West Midlands Local Section
- Gas Kinetics Discussion Group\*
- High Resolution Spectroscopy Group
- Molecular Beams and Dynamics Group\*



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# **Recollections**

## Ian's Career

2001-03 President of the Faraday Division of the Royal Society of Chemistry

2001 Head of School of Chemistry at the University of Birmingham

1995- Fellow of the Royal Society

1991- Mason Professor of Chemistry at the University of Birmingham

1989-93 Head of School of Chemistry at the University of Birmingham

1985- Professor of Physical Chemistry at the University of Birmingham

1971-85 Lecturer in Physical Chemistry at the University of Cambridge

1966-71 Demonstrator in Physical Chemistry at University of Cambridge

1965-66 ICI Research Fellow at University of Cambridge

1962-85 Fellow and College Lecturer at Christ's College, Cambridge

1972-85 Director of Studies in Natural Sciences and Chemistry at Christ's College, Cambridge

1964-65 Postdoctoral Fellow with Professor J.C. Polanyi at University of Toronto

1960-64 PhD at University of Cambridge with Thesis entitled "Fluorescence of Nitric Oxide" supervised by Dr. A.B. Callear

## **Members of the 'Smith Group' 1967—2002**

### **Research Students**

Gus Hancock  
Chris Morley  
Martin Braithwaite  
Ray Brown  
Chris Anastasi  
Paul Maw  
Rohan Fernando  
Rhobert Lewis  
David Jaffer  
Mark Howard  
David Wrigley  
John Robertshaw  
Nick Smith  
Martin Williams  
Martin Osborn  
David Klenerman

Julian de Juan  
Robert Frost  
Greg Yarwood  
Wyn Derbyshire  
Robert Baker  
Andrew Simpson  
Ian Sims  
Mike Frost  
Alistair Irvine  
Jonathan Warr  
Samantha Nimmo  
Giles Hawthorne  
Jati Salh  
Paul Sharkey  
Rowland Spencer-Smith  
Lee Herbert

Meez Islam  
Chris Moore  
David Stewart  
Gary Ward  
Michael Osborne  
Sarah Henton  
Philip James  
Alam Hasson  
Sarah Wright  
Kevin Hickson  
Delphine Chastaing  
Peter Barnes  
Simon Beach  
Paul Barrass  
David Carty  
Alejandra Paramo

### **Post-Doctoral Fellows**

Brian Ridley  
Paul Wood  
Reinhard Zellner  
Curt Wittig  
Zamik Rosenwaks  
Peter Bemand  
Barry Gelernt  
Philip Poole  
Alan Petersen  
Peter Hastings  
Graham Arnold

Jean-Yves Jezequel  
Bret Cannon  
Anita Renlund  
Joe Francisco  
David Green  
Bernard Veyret  
John Brunning  
Les Chewter  
Chris Whitham  
Markus Preidel  
Joachim Karthauser

Natalie Rowley  
Martin Klatt  
Richard Brownsword  
Joerg Weibrech  
Andrew Symonds  
Quiang Li  
Sébastien Le Picard  
Valéry Le Page  
Rouslan Olkhov  
Joel Bacon

### **Sabbatical and other Visitors**

Dick Airey  
Graham Glass  
Leon van der Merwe  
Howard Reiss

Chester Sadowski  
Christopher Davis  
Angel Gonzalez Ureña  
Adolf Miklavc

Dale Breshears  
Brian Orr  
Leon Phillips  
Xue-Feng Yang

## The Early Supervisory Years

My first contact with Ian came through the then Head of Cambridge Physical Chemistry, Jack Linnett, who visited Trinity College Dublin where I was an undergraduate to give a talk on bonding. I was so taken by this that I went to see Jack and asked if I could come to work with him in Cambridge. He told me that what he thought would be best for me was to become the first Graduate Student of an extremely bright new staff member named Ian Smith, just returned from a post doc position in Toronto, and working on the dynamics of gas phase reactions. Now that topic didn't feature heavily on the Irish Chemistry Curriculum, and when Ian sent me a long letter about what he thought I might do, and a few references to read on the topic of Infrared Chemiluminescence, my heart sank at the utter incomprehensibility of it all. My wish to go to Cambridge won over my profound ignorance of the subject, our academic marriage was arranged, and first time supervisor met up with first time supervisee in the Autumn of 1967.

Ian proudly showed me into a large laboratory containing a small infrared spectrometer. This was to be home for the next three years. He introduced me to the academic and support staff, I was warmly welcomed and I soon got the pleasant feeling that Ian had many friends in the Department, and they were soon to become mine as well. Until I met Ernie Cox, the irascible storeman, whose main aim in life was to keep his storeroom inviolate, and whose attitude to me was uncompromising. "You're a student of Smith. Smith was a student of Callear. I don't like Callear. Therefore I don't like you". What a charmer. He only became animated when talking about West Ham United, so I would make a point of going to stores on a Monday morning if his team had lost over the weekend for a satisfying wind up session.

Eighteen months of glassblowing, flow calibrations, no results and a regular sore head (from the intense literature survey of course) gave me a mid-doctorate crisis which I confessed to my supervisor. Neither Ian nor I knew what to do (we were after all academic virgins at this stage), so we had what I guess is the sixties equivalent of a male bonding session. We played squash and went to the pub. Things looked better after that.

At last the first results. I excitedly phoned Ian, and he ran down from the second floor corridor where at this early stage of his career he was still doing experiments. His enthusiasm for seeing his first supervisory success backfired. Despite my exhortations that he should not touch any piece of apparatus (as we all know, standard graduate student practice when dealing with supervisors) he did, pressed the wrong button and switched off the whole discharge flow system instead of switching it on. I suddenly experienced a surge of power. "Come back in fifteen minutes, and don't touch anything". He did, it worked, the chart recorder moved when it was supposed to do, and my Ph. D. was in the bag.

From Ian I learned to think, to have enough independence to be able to make my own mistakes, but with the back up always there from him when I wanted help. There's an art to supervision, and from my point of view Ian mastered it quickly. He gave me a great sense of academic freedom - we filled in no forms, wrote no progress reports, passed no previously charted milestones, produced no predetermined deliverables, swam through no bureaucratic treacle. Despite what would now be regarded as wanton behaviour we both remarked at a later stage that the work we had done together probably represented the best value for money in rate constants per index linked pound that either of us have achieved in our academic careers. Great days.

Gus Hancock

## The Words of a Post Doc

I first met Ian Smith in September 1971, when my wife Michele and I arrived in Cambridge to carry out postdoctoral research, her in Psychology and me in Physical Chemistry. Ian and Sue helped us settle in northwest Cambridge (Chesterton), and I began working on vibrational relaxation of CO at 77 K, modifying an existing apparatus. It was a sight to behold: a long glass tube with a lot of insulation and many one-liter LN<sub>2</sub> dewars decorating the bench top. Large cylinders of helium buffer gas were strapped to the bench, and the flash photolysis unit, I am sure, was capable of shutting down the local radio station. It was a time worth remembering. The Panton Arms received our patronage; Mr. Cox was not keen on providing the needed supplies, especially to foreigners; Reinhard Zellner and Martin Braithwaite appeared in the group; Mrs. Hurley cleaned the place, taking note of our posters; and so on.

Considering the subject matter of the paper I am presenting here, it appears that I have progressed little since 1971. For the most part this is true. My interactions with Ian shaped my future in ways that I did not appreciate at the time. It seems that he also has chosen to work at low temperatures. Maybe none of us has progressed much.

I have many, many recollections of the year that my wife and I spent in Cambridge. This period instilled in us values, habits, and friendships that have lasted a lifetime. I give myself no credit for insight in my decision to work with Ian. I was just as wild and wooly then as now, but I was extremely fortunate. Simply put, I could not have done better. My wife and I have remained close to the Smiths for over 30 years, and we cherish dearly this friendship.

Curt Wittig

## The Middle Years

My memories of Ian from his Cambridge days start where Gus' leave off. I remember clear and articulate lectures, beautifully written notes (a joy for any secretary), supervisions, and infra-red spectrometers. Ian tried to persuade me to develop a home-built interferometer to study elementary reactions (no Fourier Transforms then), but I decided that using interferometers for spectroscopy was for me, and went to do a PhD with Bill Jones. Ian became my number 2 supervisor. He tells me that I was the first student in the Physical Chemistry Department at Cambridge to have two supervisors. Collaboration was frowned upon then.

My career followed Ian's, nearly 20 years behind. I moved away, he went on sabbaticals, but we somehow seemed to find time to meet regularly on the squash court, until ..... it's a long story, ask Sue. I do not remember too much of the pubs! We started working together seriously (on science) in the early 1980s, and especially after the move to Birmingham in 1985. Ian was then moving into lasers in a big way; I remember exchanging inky hands from leaking pen recorders (no PCs then) for stained hands from dye solutions.

Throughout all the years I have known Ian, for me two qualities stand out ; he is such a nice guy, and he has complete integrity. The latter quality, alas, is not high on many people's agenda in the current UK Higher Education scene, and Ian is a beacon of what the profession should stand for. His retirement is scheduled to last one day; he is giving a seminar in Birmingham on October 2<sup>nd</sup>. No surprise to anyone here, I guess.

Richard Tuckett

## Birmingham – and Beyond

My first memories of Ian are of undergraduate lectures at Cambridge. Thermodynamics and Electrochemistry, if my memory serves me rightly. They were models of clarity, often accompanied by appropriate lecture demonstrations, a habit that Ian has continued right up to his final courses here in Birmingham, against the current regrettable trend to discourage such ‘dangerous’ practices. It was in my third year that I started to get to know Ian, when I signed up with him for a final year research project involving a highly speculative IBr photochemical laser. This never worked, but I learned some valuable lessons: (1) Ian’s projects are always very ambitious; (2) you can still get credit for research that doesn’t work if you write it up well; and (3) it is not advisable to short out a 20  $\mu$ F capacitor when fully charged to 20 kV. Despite this, I was hooked, and signed up with Ian for a PhD which started in Cambridge for a term in 1985, and moved with him to Birmingham.

I would re-echo Gus Hancock’s comments on Ian’s supervisory skills. He knew to leave well alone when things were being set up, but was always there to give advice and encouragement when needed. But when results finally started to flow, I discovered something that I am sure will have been noticed by many in the Smith group: Ian’s sixth sense for results. I hadn’t spoken to him for some time, but no sooner had the first rate constants rolled out, than he appeared at the door. This uncanny knack of sensing a working experiment has continued to the present day. Another IWMS characteristic that will be familiar to many is his ‘experimental optimism’. Ian’s ‘Some notes ...’ are legendary. These contained gems of experimental insight, but the ground that they covered was immense. Each one tended to contain at least a PhD’s worth of material!

At the end of the 80’s I moved away for a US postdoc, and Ian became Head of School. However, he still maintained an active research group, and around this time started a collaboration with the group of Bertrand Rowe, then at Meudon in Paris, and afterwards at Rennes, which was to lead to my returning to work for and then with him on the CRESU project. Following a successful joint study of neutral reaction kinetics down to very low temperatures, using British lasers and French pumps, both groups were fortunate to receive substantial funding. Ian also continued research on a number of other fronts, covering reaction dynamics and atmospheric chemistry to name but two. His standing was recognised in 1995 by his well-deserved elevation to a Fellowship of the Royal Society.

The Rennes-Birmingham collaboration has continued to this day, and in 2000 the two teams (with Ian as overall co-ordinator) were awarded the European Union’s Descartes Prize. This came during a sabbatical period for Ian in Boulder, and unfortunately coincided with Ian’s sudden and very serious illness. The final auditions for the prize had been announced, and Ian was to travel to Brussels to represent the two teams, when disaster struck. While Ian hovered at death’s door, I travelled to Brussels in his place, along with Bertrand. To my great relief we were successful, and I believe the news of the prize was a great boost to Ian as he recovered.

On a personal level, I would want to re-echo previous contributors. In particular, Ian’s qualities of honesty and integrity shine like a beacon in the current climate. I count myself greatly privileged to have had Ian as a teacher, supervisor, colleague, mentor and friend. My very best wishes are with Ian and Sue as they embark on this new period of their lives.

Ian Sims

## Messages From Absent Friends

Message: Dear Ian and Sue: My very best wishes and congratulations to you both for reaching this landmark in such a happy and healthy condition. You both have made a wonderful contribution to the human side of science, for myself and I'm sure for many other people in our field. I hope to see you at more conferences in the future and know that the knowledge gained in your lab will be discussed and appreciated at those conferences for many years to come.

David Parker, University of Nijmegen, Netherlands

---

Message: Dear Ian, I am truly sorry that I cannot attend the conference in your honour. The many famous people speaking at the conference bear witness to the major contribution you have made to the field of atomic and molecular collisions and reactivity over a long and productive period. With best wishes for the future.

Professor Gabriel Balint-Kurti, University of Bristol, U.K.

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Message: Firstly, sorry that I can't attend the "doo" but that I can write a message is just super - and this from a Luddite. And secondly, not really, there is little to say except THANKS for all the great stuff, the contributions and the many ideas that made all of us think just a bit more. It never hurts! And enjoy the future! And that is not anecdotal.

Allan Laufer, Team Leader, Fundamental Interactions, Office of Basic Energy Sciences, USA

---

Message: Dear Ian and Sue: Congratulations, Ian, on an illustrious and distinguished career. We know, Sue, that he couldn't have done it without your constant love and support. Your friendship has brightened our lives. All our best wishes are with you as you begin a new and exciting phase of your lives together. Love, Dale and Linda

Dr. Dale Breshears, Los Alamos Natl. Lab. (Retired), USA

---

Message: Dear Ian, I wish you and Sue the best on the occasion of your retirement and the celebration of your eminent scientific career, taking place in Birmingham. It has been a pleasure to interact with you scientifically, although I never had the opportunity to collaborate with you and actually co-write a paper. Our research intersected several times in odd ways, and we did work nearly simultaneously on the same systems, viz. the CN + O<sub>2</sub> and H + NO<sub>2</sub> reactions. I certainly benefited from these "competitions" and trust that you did so also. I hope that you will have many more productive years in whatever endeavors you undertake.

With best wishes, Paul J. Dagdigian, Johns Hopkins University, Baltimore, MD, USA

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Message: Looking at Ian's jolly smugness depicted on the conference website emphasises how disappointed I am to find myself on the other side of the world while Ian, Sue and so many of our mutual friends and colleagues are celebrating in Birmingham. We all have much to celebrate - not Ian's retirement (which we have yet to see and believe!), but more the positive influence he has had on our lives through his science, his dependability and rigour, his rugged determination (I'm told that Yorkshiremen are like that) and his generosity and friendliness. My own experiences of Ian comprise many encounters through the journal pages but all too few face-to-face meetings at conferences, two or three brief visits to Cambridge and Birmingham, and one memorable visit when we were able to have Ian out in Australia at one of our RACI Physical Chemistry Division conferences (on which occasion, science apart, I remember his fierce resolve

on the tennis court and my taking him to Sydney Airport via Sydney's famous Bondi Beach where I forced him to brave the surf before I would let him on the plane). Why am I addressing you in the third person, Ian? I haven't mentioned the four or five months when we really got to know each other, soon after your arrival in Birmingham. Marilyn, Kirsten, Bronwyn and I remember with great pleasure all the kindness and hospitality that you and Sue (and others, too – the Tucketts especially) offered us during our stay in Birmingham. When are you going to give us a chance to return such great hospitality? Just think of what you could be doing at our new Hawks Nest seaside holiday house at a time of year when the frosty air is hovering around Cambridge. We could even talk some science, too! All the best, Ian and Sue. We wish you a healthy, busy, happy life back in Cambridge and we look forward to further pleasant interactions with you both in the years ahead.

Brian Orr (and Marilyn, too), Macquarie University, Sydney, Australia

P.S. Please note that I didn't mention the cricket!

---

Message: Dear Ian and Sue, I hope you enjoy the conference, the final year in Birmingham and your move back to Cambridge. I was Ian's third (?) graduate student about 30 years ago. Anecdotes - (i) CSe2 and the old Cambridge news head line "Drains Exonerated: Science the Sinner" (ii) the curious case of the missing canary/ CO detector (iii)open day in the stores when Ernie Cox was on leave Best Wishes, Martin & Paula Braithwaite

Professor Martin Braithwaite, Cranfield University, UK

---

Message: Dear Ian, unfortunately, business is keeping me away from the meeting which I very much would have liked to attend. Anyway, all the best to you and Sue, and please give my regards to Ian Sims, Bertrand Rowe, Reinhard Zellner and Juergen Troe. - Joachim PS: you might consider inviting Reinhard Zellner for a beer or two: The first CRESU LIF signals from the wind tunnel in Paris were obtained with a photomultiplier tube and some quartz lenses from RZ's secret storage. I never told Reinhard - to be sure, I placed the tube and lenses back into RZ's cupboard after use. As you are a very honest gentleman, I would not occur to me to blame you for forcing a post-doc to temporary theft, but, having said that, you did not really give me an appropriate budget either. Have a great time!

VP Joachim Karthaeuser, Adsphere - NKT Research&Innovation, Denmark

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Message: Dear Ian and Sue best wishes for you for the new challenges. Please accept our apologies for not being there due to longstanding commitments in the Far East which have resulted in this Round the World trip. Our thoughts have been with you. We trust that the meeting has been very successful end. Sor for now: Greetings from HongKong Klaus and Helen

Professor Klaus Muller-Dethlefs, The University of York, UK

# **Invited Talk**

# **Abstracts**

# The Long Saga of the NO Molecule

M. Alexander

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More than 20 years ago Sudbø and Loy initiated the study of inelastic scattering of the NO molecule.<sup>1</sup> Since then, collisions of NO with noble gasses have become the paradigm for state-resolved rotationally energy transfer. This has culminated in two recent papers in *Science*, in which imaging techniques have been used to determine angle and polarization resolved cross sections for collisions of NO with Ar.<sup>2</sup> Spectroscopic investigation of the NO–Ar van der Waals molecule goes back to work by Howard and his students in the 1980's.<sup>3</sup> More recently, Meyer, Softley and their students<sup>4,5</sup> have used two-photon techniques to study the lower bend-stretch levels of the NO–Ar and NO–Ne complexes.

Because of the open-shell character of the NO molecule, collisions involve motion on two potential energy surfaces.<sup>6</sup> Pack and co-workers carried out the first theoretical study of the NO–Ar potential energy surfaces in 1977.<sup>7</sup> We developed the correct quantum framework for the scattering dynamics,<sup>6,8</sup> and have subsequently published a series of quantum studies of collisions of NO with both Ar and He.

Of all the collision studies, the only accurate measurement of absolute cross sections, which is a critical test of the accuracy of any potential energy surface, is the CRESU work of Smith and his co-workers.<sup>9</sup>

We shall review the extensive work on the NO–Ar system and attempt to focus on remaining areas of interest.

- [1] A. S. Sudbø and M. M. T. Loy, *Chem. Phys. Lett.* **82**, 135 (1981)
- [2] K. T. Lorenz, D. W. Chandler, J. W. Barr, W. Chen, G. L. Barnes, and J. I. Cline, *Science* **293**, 2063 (2001); H. Kohguchi, T. Suzuki, and M. H. Alexander, *ibid.* **294**, 832 (2000).
- [3] P. D. A. Mills, C. M. Western, and B. J. Howard, *J. Phys. Chem.* **90**, 4961 (1986); **86**, 3331 (1986).
- [4] J. Fleniken, Y. Kim, and H. Meyer, *J. Chem. Phys.* **109**, 8940 (1998); Y. Kim, J. Fleniken, H. Meyer, M. H. Alexander, and P. J. Dagdigian, *ibid.* **113**, 73–85 (2000); Y. Kim, J. Fleniken, and H. Meyer, *ibid.* **114**, 5577 (2001).
- [5] O. L. A. Monti, H. A. Cruse, T. P. Softley, and S. R. Mackenzie, *Chem. Phys. Lett.* **333**, 146 (2001).
- [6] M. H. Alexander, *Chem. Phys.* **92**, 337 (1985).
- [7] G. C. Nielson, G. A. Parker, and R. T. Pack, *J. Chem. Phys.* **66**, 1396 (1977).
- [8] M. H. Alexander, *J. Chem. Phys.* **76**, 5974 (1982); T. Orlikowski and M. H. Alexander, *ibid.* **79**, 6006 (1983).
- [9] P. L. James, I. R. Sims, and I. W. M. Smith, *Chem. Phys. Lett.*, **272**, 412 (1997); P. L. James, I. R. Sims, I. W. M. Smith, M. H. Alexander, and M. Yang, *J. Chem. Phys.* **109**, 3882 (1998).

# **Chemical Reactions at Low Temperatures: Has Theory Inspired Experiments?**

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This talk will review some theoretical predictions of rate constants for chemical reactions at low temperatures. Emphasis will be placed on reactions of particular interest to Ian Smith – chemical reactions between neutral radicals. It will be shown that although simple quantum “capture” theory has been very useful for predicting the rates of ion-molecule reactions, the theory has not been so successful for reaction involving neutrals. Quite often a detailed calculation of the potential energy surface followed by detailed dynamics calculations is required. However, the capture theory has provided some useful predictions on the temperature dependences of fast reactions that have stimulated new experiments and does provide an upper bound to the rate constant at low temperatures.

Recent ideas on extending quantum dynamics theory to fast unimolecular reactions will also be described with an application to the formation of ozone.

# **Bond-Selective Bimolecular Reactions of vibrationally Excited Molecules**

F. Fleming Crim

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Vibrational excitation permits the selective control of the pathways of bimolecular reactions. Exciting a stretching vibration of a bond to a light atom, such as C-H, N-H, or O-H, places energy in a degree-of-freedom that often possesses a large component of motion along the reaction coordinate in a H-atom abstraction reaction. Examples are the reaction of vibrationally excited H<sub>2</sub>O, HNCO, and CH<sub>4</sub> with a variety of atoms such as H, Cl, and O. The simplest spectator model of the reaction, which predicts its substantial acceleration, often describes the experimental observations well, and it is possible to use such vibrational excitation to steer the course of the reaction. More subtle aspects of the nature of the initially prepared vibrational state, its perturbation during the reactive encounter, and the identity of the reaction coordinate play a significant role and require a more elaborate picture of the vibrationally driven chemistry.

# Cold collisions of electrons and molecules

David Field<sup>1</sup>, Nykola Jones<sup>1</sup>, Jean-Pierre Ziesel<sup>2</sup>

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<sup>2</sup> LCAR - IRSAMC Université Paul Sabatier, Toulouse, France

Cold electron collisions give a special insight into the nature of quantum scattering, since these cold encounters, in which the de Broglie wavelength of the impacting particle is very greater than the dimensions of the target, emphasize the coherent wave nature of matter. The field of cold collisions is one in which particles pass ghost-like through each other, or are strongly scattered through the intervention of classically unattainable states, or alternatively through a superposition of energetically forbidden trajectories, each in a manner alien to a classical vision of natural phenomena. Cold electron collisions have the additional attraction that they occur in the natural world, in planetary atmospheres and in the interstellar medium, as well as in industrially important plasmas for device fabrication.

In this brief review, I will describe some experiments performed with electron beams in the energy range of a few meV to a few hundred meV, with an energy resolution of 0.65 meV to 1.75 meV. A great variety of species has been studied, ranging from the simplest diatomics to more complex molecules such as benzene, hexafluorobenzene and still larger species such as naphthalene or anthracene. Scattering data have revealed a number of fascinating quantum phenomena, some known or strongly suspected from theory, others unknown and which remain largely unexplained.

I will dwell on recent results relating to the nature of virtual state scattering, for example in CO<sub>2</sub>, with special reference to the lifetimes of electron-molecule collision complexes. I will also discuss the case of electron collisions with CS<sub>2</sub> in which giant resonances have been found at very low energy.

# REMPI-LIF Studies of Ion-Molecule Reactions

Michael J. Frost

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Ion-molecule reactions are of widespread importance in a range of weakly-ionised plasma environments including electrical discharges and the terrestrial atmosphere at high altitudes. Further, these reactions are of fundamental interest since the collisional potential energy surfaces generally possess at least one energy minimum of significant magnitude owing to the electrostatic attraction between the ion and the molecule. Commonly, this well-depth is somewhere intermediate between the energy of a covalent and a non-covalent bond. For this reason, it is of interest to investigate the effect of this attractive well on the properties of a range of ion-molecule reactions.

Whilst laser-based techniques have been routinely applied to experimental studies in neutral chemistry, they have not been widely used to study ion-molecule reactions. For example, in ion chemistry, kinetic measurements are commonly performed using flow tube techniques coupled with mass spectrometric detection. However, the use of flow tubes has a number of disadvantages. First, the range of total pressure over which measurements can be conveniently made is usually restricted owing to the requirement for laminar flow in the tube. Second, only indirect methods can be used to study the reactivity of ions possessing internal excitation. In this talk, I will describe the use of a laser based technique in which ions are produced by Resonance Enhanced Multiphoton Ionisation (REMPI) and detected by laser-induced fluorescence. Recent results on the  $\text{N}_2^+ + \text{N}_2$ ,  $\text{O}_2$  and  $\text{O}$  reactions will be presented.

# Time Resolved Infrared Emission: An Academic Comfort Blanket

Gus Hancock

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Ian Smith taught me the technique of infrared chemiluminescence in the late 1960s. The early methods, borrowed from John Polanyi, involved observations of spectrally resolved emission from the products of a chemical reaction in a continuous flow system, and of the quenching of this emission by vibrational energy transfer brought about by the addition of various gases. Relative rates were found from Stern Volmer plots, with the Einstein A coefficients providing the time variable needed to extract rate constants. Proper time resolution seemed a difficult task then.

Lasers and Fourier transform methods have changed that. The combination of laser initiation of chemical processes and time resolved observation of the resultant emission by means of step scan interferometry means that processes can be observed on a time scale dependent only on the detector response (normally in the  $\mu$ s range), with A coefficients as low as  $1\text{ s}^{-1}$ , and from concentrations of strongly emitting species of the order of  $10^{10}\text{ cm}^{-3}$ . Information can be gained on kinetics of removal and energy transfer, on the vibrationally and rotationally excited product distributions and in some cases on the quantum yields of reaction products. As all emitting species are seen in the same experiment, the technique has the added advantage that removal of vibrational energy from a donor can be seen at the same time as the appearance of vibrational excitation in an acceptor.

In this talk we give some recent examples. Energy distributions will be presented for the NO product of the reaction between  $\text{O}({}^1\text{D})$  and  $\text{N}_2\text{O}$ , and the vibrational dependence reported of the rate constant for relaxation of  $\text{NO}(\text{v})$  with  $\text{N}_2\text{O}$ . Similar types of result on the initial distribution of the  $\text{NO}(\text{v})$  photofragment from dissociation of  $\text{NO}_2$  at 248 nm, and on its resultant collisional behaviour will be described. Observation of emission from the products of the reactions of  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  radicals with  $\text{NO}_2$  have allowed rate constants to be determined, and the use of this emission as a marker for  $\text{CF}_3$  loss in the presence of  $\text{O}_2$  gives the rate constant for the recombination process. Reactions of singlet and triplet methylene have also been observed, and results on the product channels in the reactions with  $\text{O}_2$  will be described. The results demonstrate that an enjoyable Ph.D. project never gets forgotten, and that a great deal of comfort can be extracted from returning to a technique first learnt in academic childhood.

# Interstellar and Circumstellar Chemistries: The Role of Neutral-Neutral Reactions

Eric Herbst

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Over 100 different molecules have been detected in the gas phase of cold (10 K), “dense” ( $10^4$  cm $^{-3}$ ) interstellar clouds. Comprised of gas and tiny dust particles, these heterogeneous clouds are the birthplaces of stars and planetary systems, and are of great interest to astronomers. Much of what we know about the current conditions in dense clouds, including the process of star formation, derives from spectroscopic observations of the many molecules present. A detailed understanding of the history of such regions also requires a true understanding of the chemical processes that form and destroy molecules under the cold and low-density conditions present. Although it was once thought that the gas-phase chemistry is totally dominated by ion-molecule reactions, it is now known, thanks to the work of Ian Smith, Bertrand Rowe and their colleagues, that neutral-neutral reactions also play a key role. The extent of this role is still incompletely understood. On the other hand, in carbon-rich circumstellar sources, neutral-neutral reactions are known to play a large and possibly dominant role in the production of large organic molecules.

# Using Semiclassical Theory to Include Quantum Effects in Classical Molecular Dynamics Simulations

William H. Miller

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Semiclassical (SC) theory provides a very good description of essentially all quantum effects in molecular dynamics; this has been long appreciated and validated by many applications to small molecular systems [cf. *Adv. Chem. Phys.* **25**, 69-177 (1974)]. Since SC theory is built on the classical trajectories of the dynamical system, it should in principle be possible to use it also to add quantum effects to classical trajectory simulations of *complex* molecular systems (i.e., those with many degrees of freedom), e.g., chemical reactions in solution, clusters, proteins, or any complex environment. The practical implementation of SC theory for complex systems is based on various initial value representations (IVRs), which have recently undergone a re-birth of interest in this regard. This talk reviews the basic idea of the SC-IVR approach and describes a variety of recent applications that have been carried out using it. [For a recent review, see *J. Phys. Chem. A* **105**, 2942-2955 (2001).]

# Not-So-Statistical Reactions

C. Bradley Moore

*Ohio State University, USA*

Three experiments aimed at understanding unimolecular reaction dynamics for systems that exhibit non-statistical behavior will be described.

1. Femtosecond ir multiphoton dissociation of diazomethane has been accomplished in collaboration with K.L. Kompa's group. Part of the singlet methylene is produced on a sub-picosecond timescale, faster than RRKM, when the CNN asymmetric stretch is excited.
2. The photodissociation of vinyl following excitation of its first excited electronic state has been studied by REMPI imaging of the H fragment. Dissociation occurs rapidly compared to migration of H between carbons.
3. Fluorescence-excitation, dispersed-fluorescence (with T. Miller's group), and SEP spectroscopy of methoxy and its dideutero isotopomer have been carried out to characterize the molecular states near the dissociation threshold of  $8,000\text{ cm}^{-1}$ .

# Radical Kinetics in Combustion and Atmospheric Chemistry

Mark Blitz, Kevin Hughes, Kenny McKee,  
Mike Pilling, Struan Robertson and Paul Seakins

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Rate coefficients and product yields for elementary reactions are essential components of chemical mechanisms used in models of combustion and atmospheric chemical processes. It is increasingly recognized that it is necessary to combine measurements and models of reaction rates in order to provide rate data of the required accuracy under the conditions appropriate to the application. Several reaction systems will be examined to illustrate recent investigations at Leeds:

1. The measurement of product yields presents a substantial challenge to experimentalists. We have used vuv LIF to study the formation of H in reactions of CH and  $^1\text{CH}_2$ . The yields are placed on an absolute basis by comparing the LIF signal from the target reaction with that from a reaction with a well established H atom yield. The reactions of CH with hydrocarbons have been investigated, using  $\text{CH} + \text{CH}_4$  as the reference reaction. The reactions involve insertion into a C-H bond, followed by fragmentation of the resulting radical. The results can be rationalized on the basis of the radical potential energy surface. For  $^1\text{CH}_2$ , the reaction with  $\text{H}_2$  is used as the reference. The most striking result is the demonstration that reaction with  $\text{O}_2$  leads exclusively to collision induced intersystem crossing.
2. Reactions of vibrationally excited OH with  $\text{SO}_2$  and  $\text{C}_2\text{H}_2$  have been employed to determine the limiting high pressure rate coefficient for association reactions. There are significant discrepancies, however, with direct high pressure measurements and, furthermore, the rate coefficients for  $\text{OH} + \text{C}_2\text{H}_2$  depend on the degree of vibrational excitation. The results and their implications will be discussed.
3.  $\text{H} + \text{SO}_2$  is the major route for  $\text{SO}_2$  removal in flames. The reaction proceeds via the intermediates  $\text{HSO}_2$  and  $\text{HOSO}$ , and the high temperature products are  $\text{OH} + \text{SO}$ . Experimental and theoretical investigations of the reaction will be described and the implications for combustion systems discussed.

# **Reaction Dynamics a Molecule at a Time; Thermal, Photo-induced and Electron-induced Reaction of Adsorbates on Si, by STM**

John C. Polanyi

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Heat, light and low-energy electrons have been used to induce reactions between sub-monolayers of halides and Si(111)7×7 or Si(100)2×1 substrates. The reaction dynamics were inferred from the alteration in the STM images of the individual molecules, due to the stimulus. Reagents were benzene, halobenzene, and multiply halogenated benzenes. The molecules were observed to desorb, diffuse to new sites, change their state of attachment, or undergo fragmentation accompanied by localised reaction with the substrate. These findings have been examined by ab initio calculations, also reported.

The experiments were performed by Duncan Rogers, Harikumar Rajamma and Nan Li, and the theory by Guo-Ping Jiang and Fedor Y. Naumkin, all at the University of Toronto.

# From the Strong to the Weak: OH-Molecule Adducts and Their Impact on Kinetics and the Atmosphere

A. R. Ravishankara

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80309 USA*

The OH radical can form adducts with many molecules. The "adduct" could be very strongly bound ( $\Delta_rH^{\circ}>20$  kcal mol<sup>-1</sup>), and thus lead to a "stable" molecule via the association reaction. The adduct can be very weakly bound, essentially via hydrogen bonding, and then go on to yield products. Yet, the formation of the weakly bound adduct, in what were once thought to be direct abstraction reactions, can affect the kinetics (and products?) of the reaction and the course of the degradation of a molecule of interest in the atmosphere. There can be adducts with intermediate bond strengths, which can lead to new reactions. All of these adducts can alter the course of the reaction and thus have different effects on the atmosphere. I will describe a few such adducts, their impact on the kinetics of the reaction, and their role in the chemistry of atmosphere.

# **The Chemical-Oxygen Iodine Laser: Exploitation of the Magic Oxygen Singlet Delta Molecule - a Status Report**

B.D. Barmashenko, E. Bruins, D. Furman, A. Katz,  
V. Rybalkin and S. Rosenwaks

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The chemical oxygen iodine laser (COIL) is the only known example of a high power chemically driven electronic transition laser. Despite many years of research and development, several aspects of the chemistry and fluid dynamics processes occurring in COIL systems are not properly understood. Dissociation of  $I_2$  by singlet  $O_2$ , the process that generates the lasing species, is a critical step that is not well understood. This process has a dramatic influence on the efficiency of the laser. Another important process is the mixing between singlet oxygen and iodine. To achieve high lasing power the mixing efficiency should be high. Thus, it is very important to know how the mixing efficiency depends on the iodine injection scheme and for what mixing scheme maximum mixing efficiency could be achieved. To understand the kinetic and mixing processes in COILs it is necessary to carry out detailed diagnostic studies of the COIL active medium including measurements of  $I_2$  dissociation fraction and densities of different species ( $I^*$ ,  $O_2(^1\Delta)$ ,  $O_2(^3\Sigma)$  and  $H_2O$ ) as a function of the distance along and across the flow and the flow rates of different reagents. On the other hand, reliable models should be developed describing the COIL operation and, in particular, the small signal gain, iodine dissociation fraction and gas temperature in the resonator. Comparison between experimental and theoretical results could establish the kinetic scheme for  $I_2$  dissociation and the values of the rate constants of reactions involved in this scheme. We report on the measurements of spatial distributions of the gain and temperature across the flow in a slit nozzle supersonic COIL using diode laser based diagnostic systems. Currently available models are compared to the experimental results and new directions in COIL research are discussed.

# Obtaining Molecular Data for Astrochemistry with the CRESU Technique.

B.R. Rowe

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Although molecular species like the CN radical were observed in interstellar medium more than fifty years ago, it is mostly in the last three decades that, thanks to the development of radio astronomy, a large number of molecules have been detected in various interstellar environments, most of them in huge aggregates of matter (molecules and dust) known as dense interstellar clouds. These clouds are the birth place of stars and planets through a process of gravitational collapse, and as such, are objects of first importance in astrophysics. To understand how molecules can be synthesised in the extreme conditions of these clouds (temperature as low as 10 K, molecular concentration of typically  $10^4$  molecules  $\text{cm}^{-3}$ ) is clearly a fascinating question. Beside this chemical aspect it is also of first importance for the interpretation of observation to understand the various molecular processes which govern the characteristics of the lines emitted by interstellar molecules in the long wavelength range of the spectrum, for example rotational and spin-orbit state excitation and relaxation.

The experimental investigation of molecular processes, either chemical or physical, at the very low temperatures relevant for interstellar clouds, was and is still a challenge. The CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) was devised in the early eighties to study ion-molecule reactions down to temperatures as low as 8 K. In the last decades, thanks to a very enjoyable collaboration with Ian and the Birmingham group it has been extended to neutral-neutral reactions and a variety of other molecular processes. The results concerning neutral-neutral reactions have resulted in a large change in the current views of interstellar gas phase chemistry.

In this talk I will review some of the most recent work performed with the Rennes CRESU including chemistry of silicon atoms and electron attachment processes. I will also briefly present some future plans of experiments concerning radical-radical reactions and the study of very condensable species such as Polycyclic Aromatic Hydrocarbons.

# Low Temperature Molecular Collisions

## The CRESU Technique and Applications to Astrochemistry

Ian Sims

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Molecular spectroscopists have long benefited from the advantages of dramatic cooling by the use of free jet expansions and molecular beams. Those interested in molecular collision dynamics have not, in general, been so fortunate. The crossed molecular beam technique has many advantages, but in general it is unable to explore the regime of very low collision energies, and internal state distributions can often be inefficiently relaxed. Cooled cells are limited by the vapour pressure of the species under study.

The advent of the CRESU technique (CRESU is a French acronym, standing for Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) combined with laser photochemical techniques has in recent years revolutionised the study of reaction kinetics and molecular energy transfer at low temperatures, down to around 10 K. By employing specially profiled Laval nozzles, a relatively high density ( $10^{16}$ – $10^{18}$  cm<sup>-3</sup>) and very low temperature (7–220 K) gas phase environment can be created. The resulting uniform supersonic flow operates under thermalised and yet highly supersaturated conditions, making it ideal for the study of very low temperature molecular collisions under well-defined conditions.

A full description of the CRESU technique will be given, and recent work in the area of low temperature reaction kinetics and energy transfer will be reviewed. Emphasis will be placed on the application of the CRESU technique to processes of astrochemical interest, including the important interstellar reactions of C(<sup>3</sup>P) with C<sub>2</sub>H<sub>2</sub> and O(<sup>3</sup>P) with OH, as well as astrophysically important energy transfer processes such as the collisional relaxation of atomic fine structure states in C(<sup>3</sup>P) and Si(<sup>3</sup>P).

# Statistical Adiabatic Channel and Classical Trajectory Calculations for Reactions of Astrophysical Importance

Jürgen Troe

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Among chemical reactions of interstellar importance, barrierfree capture processes play an important role. This talk describes the theoretical analysis of radical-radical and ion-molecule capture in terms of classical trajectory and quantum statistical adiabatic channel calculations. Among the examples considered are processes such as  $O + OH \rightarrow O_2 + H$ ,  $OH + OH \rightarrow H_2O_2$ , and  $NH_3 + NH_4^+ \rightarrow N_2H_7^+$ . It is shown under which conditions the transition from classical to quantum behaviour takes place. Also the role of open electronic shells is illustrated. Finally, pressure dependences in combination processes from CRESU experiments are analyzed.

# Local Quantum Chaos in Helium Nanodroplets

E. Polyakova, D. Stolyarov, X. Zhang, V. V. Kresin, and C. Wittig

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A mass spectrometer depletion spectrum in the region  $17,700 - 18,300 \text{ cm}^{-1}$  has been recorded for  $\text{NO}_2$  embedded in superfluid (0.37 K) helium nanodroplets. Gas phase  $\text{NO}_2$  is vibronically chaotic at these energies. Transitions are broadened and blue-shifted relative to their gas phase counterparts. The spectrum is fitted satisfactorily with widths and shifts that are both  $\sim 7 \text{ cm}^{-1}$ . Modest dispersions (*i.e.*, 90% lie within  $2 \text{ cm}^{-1}$  of the central values) are consistent with quantum chaos in  $\text{NO}_2$ . Relaxation is dominated by interactions of  $\text{NO}_2$  with its non-superfluid helium nearest neighbors.

# Atmospheric Gas Phase / Particle Interactions: Concepts, Techniques and Results

Reinhard Zellner\*

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The interactions of atmospheric trace gases and free radicals with dispersed liquid or solid surfaces in the atmosphere has become an important topic of atmospheric sciences. This is because such interactions have substantial impact on atmospheric composition including oxidant levels, radiative properties or else.

As compared to gas phase chemistry atmospheric multiphase chemistry is still in its infancy. Neither concepts /theory of gas surface interactions nor techniques for study of elementary processes are developed far enough to make suitable extrapolations into regimes well outside that of study. This is a result of an enormous complexity of the condensed phases with respect to chemical composition, physical properties and surface morphology.

Heterogeneous atmospheric reactions are conventionally described by reactive uptake coefficients which are overall first order rate coefficients encompassing a number of elementary processes including accommodation, phase transfer and transport. Moreover, reactive losses are also influenced by thermodynamic quantities such as Henry coefficients and/or adsorption equilibria.

In this paper we describe recent advances in the development and application of laboratory techniques to study gas/surface interactions of atmospheric relevance as well as their motivations with respect to increased resolution in elementary conceptual approaches. We will discuss selected results from studies using the following techniques: (1) Knudsen cell/QMS for study of the uptake of NOy species on mineral dust and soot surfaces, (2) DRIFTS studies of uptake rates of NOy on ice and acid hydrate surfaces and, finally, (3) Optical Levitation / Raman-Mie analysis of single micro droplets.

\* Co-authors: C.Mund, S.Seisel, E.P.Röth, S.Wagner, H.Reinhardt and P.Behr

# **Poster Abstracts**

# Structure of Monolayer Dye Films Studied by Brewster Angle Cavity Ringdown Spectroscopy

Dr. Andrew J. Alexander

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Cavity ringdown spectroscopy (CRDS) has proven enormously successful for very sensitive absorption measurements of gas-phase species. So far, however, there have been very few studies of CRDS for liquid or solid species.

We report CRDS measurements of thin films of oxazine 1, oxazine 170 and malachite green dyes deposited on borosilicate substrates. The method involves insertion of the substrate into a 2-mirror cavity at Brewster's angle to reduce reflection losses. Using this technique, we were able to measure monolayer and sub-monolayer quantities of dye. The minimum observed concentration of malachite green in the present work was calculated to be  $\sim 1.1 \times 10^{-8}$  mol m<sup>-2</sup> (equivalent to  $8.3 \times 10^{10}$  molecules illuminated in our cavity). The results show that the surface causes minor solvatochromic shifts, consistent with the existence of polar silanol end-groups on the borosilicate surface. The surface was also found to induce dimer formation of the dyes: at surface coverages of  $\sim 2.8 \times 10^{-7}$  mol m<sup>-2</sup>, the ratio of malachite green dimers to monomers was estimated as  $C_d/C_m = 0.22$ .

# Relaxation of Highly vibrationally Excited H<sub>2</sub>O(04><sup>-</sup>) in Collisions with H<sub>2</sub>O, Ar, H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>

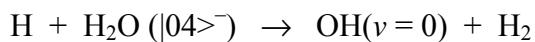
P.W. Barnes, Ian R Sims and Ian W.M. Smith

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We have previously reported how comparisons of the yields of OH from the reaction of H<sub>2</sub>O in the vibrational level, |04><sup>-</sup>, and photodissociation of the same water molecules at 266 nm could be used to determine the branching ratio between reaction and vibrational relaxation of H<sub>2</sub>O(04><sup>-</sup>) in collisions with H atoms. The experiments involved the preparation of water molecules in specific vibrational levels *via* high overtone pumping, using a tuneable dye laser, and the detection of the OH reaction or photodissociation product via laser-induced fluorescence (LIF), using a tuneable ultraviolet laser.

In the present work, this method has been adapted in order to measure rather directly the collisional removal of H<sub>2</sub>O(04><sup>-</sup>) in collisions with a variety of partners. Molecules are prepared, as before, in the (04><sup>-</sup>) state using the tuneable pump laser operating at *ca.* 720 nm. These molecules can be selectively photodissociated at 266 nm, using the frequency-quadrupled output from a Nd:YAG laser, and the OH radicals that are produced can be detected by LIF using the ultraviolet probe laser.<sup>2</sup> In the current experiments, we keep a fixed short delay between the pulses from the photolysis and probe lasers and vary the time delay between these laser pulses and that from the pump laser. In this way, the LIF signals from OH map the decay of water molecules from the (04><sup>-</sup>) state.

Results are reported in Table 1 for the relaxation of H<sub>2</sub>O(04><sup>-</sup>) in collisions with H<sub>2</sub>O, Ar, H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. The implications of the data will be discussed both (a) in respect of our earlier results on the state-selected kinetics of the reaction



and (b) in relation to the possibility that photodissociation from high vibrational states of H<sub>2</sub>O might provide an additional source of OH radicals in the Earth's atmosphere.

**Table 1** Rate coefficients ( $k_{relax}$  / cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for relaxation of H<sub>2</sub>O (04><sup>-</sup>) in collisions with H<sub>2</sub>O, Ar, H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>

	$k_{relax}$ / cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
H <sub>2</sub> O	$(4.1 \pm 1.2) \times 10^{-10}$
Ar	$(4.9 \pm 1.1) \times 10^{-12}$
H <sub>2</sub>	$(6.8 \pm 1.1) \times 10^{-12}$
N <sub>2</sub>	$(7.7 \pm 1.5) \times 10^{-12}$
O <sub>2</sub>	$(6.7 \pm 1.4) \times 10^{-12}$

# Rotational Energy Transfer in Collisions of Jet-Cooled NO( $X^2\Pi_{1/2}$ , $v = 0$ ) with Ar and with He: Energy and Angular Momentum Constraints

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Using a crossed molecular beam apparatus with pulsed supersonic sources that can be rotated with respect to one another, we have examined rotational energy transfer in collisions of NO, cooled predominantly into the ( $^2\Pi_{1/2}$ ,  $v = 0$ ,  $j = 0.5$  and 1.5) rovibronic levels, in collisions with Ar and with He at several selected energies. Relative values of the populations transferred into specific final states ( $^2\Pi_{1/2}$ ,  $v = 0$ ,  $j_f$ ) have been determined by recording laser-induced fluorescence spectra of NO from the region where the beams intersect. Results are reported for the following collision energies: NO—Ar, 265, 514, 720 and 980  $\text{cm}^{-1}$  and NO—He, 260, 530, 784 and 963  $\text{cm}^{-1}$ . In both cases, the distribution over final rotational states is wide with the cross-sections decreasing with increasing  $\Delta j$ . The average energy transferred from relative translational motion to rotation in NO is approximately independent of collision energy, corresponding to 16.5% in the case of NO—Ar, and 10.5% for NO—He. Moreover, the final state distributions clearly show the effects of two different constraints: the need to conserve both energy and angular momentum. In NO—Ar collisions, transfer takes place to essentially all energetically accessible final states,  $j_f$ . This is not the case for NO—He, where the smaller range of orbital angular momenta leads to a lower limit to the highest  $j_f$  state.

The results are compared with the results of model calculations in which energy is assumed to be transferred impulsively at ‘hard’ surfaces whose dimensions were derived from *ab initio* calculations on the NO—Ar and NO—He systems. For NO—He, the agreement between the results of the experiments and these model calculations is good, confirming that, in these collisions in which the spin-orbit state of the NO is preserved, energy is transferred through the action of repulsive forces and that the difference between the results for NO—Ar and NO—He can be put down to the operation of momentum constraints in the latter case. In the case of NO—Ar collisions, the agreement between the experimental results and the model calculations is less good. This discrepancy is attributed to the fact that, when the first impulsive collision transfer large amounts of angular momentum to the NO molecule, the partners may undergo a secondary collision before they separate.

# Neutral-Neutral Reaction Kinetics of Atoms at Very Low Temperature

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The study of neutral-neutral reaction kinetics made a remarkable breakthrough about 10 years ago when new experimental techniques became available for exploring the behaviour of such processes at very low temperatures. At the origin of this was a fruitful discussion between Professor I.W.M. Smith and B. Rowe in order to adapt the CRESU technique to the study of radical-molecule reactions. An exceptionally valuable collaboration was born between the University of Birmingham and the University of Rennes which is still strongly active.

The CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus based on the uniform supersonic expansion of a buffer gas, was originally dedicated to the measure of ion-molecule rate coefficients at temperatures as low as 8K. Associated to pulsed laser techniques it then became a very powerful tool for the study of radical-molecule reactions at temperatures below 100K. First results were obtained in April 1992 regarding the CN + O<sub>2</sub> reaction confirming the negative temperature dependence of the rate coefficient found by Sims and Smith, (CPL, 151, 481 (1988) ) at temperatures higher than 100 K and extending this behaviour down to 13 K. Since then, more than 40 neutral-neutral reactions were studied either in Rennes or in Birmingham where a twin apparatus was commissioned in 1995. These include reactions involving molecular radicals such as CN, OH, CH or C<sub>2</sub>H and atoms such as Al, Si, C and B.

The present contribution will focus on atom-molecule reactions that were studied in Rennes, namely: Al + O<sub>2</sub>, Si + O<sub>2</sub>, NO, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> and B + O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. When available, theoretical results will be compared to the experimental results obtained using the CRESU apparatus.

# The Interstellar O<sub>2</sub> Problem: Low Temperature Rate Coefficients for the O(<sup>3</sup>P) + OH Reaction

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Along with H<sub>2</sub>O and CO, O<sub>2</sub> is thought to be a major reservoir for elemental oxygen in dense interstellar clouds. The O(<sup>3</sup>P) + OH reaction is the dominant process for the production of O<sub>2</sub> in this environment. Recent attempts to detect O<sub>2</sub> using ground and satellite observation techniques have failed. This has lead to upper limits being placed on its abundance that are much lower than expected from chemical models.

It has been speculated that a slower than expected rate coefficient for the O(<sup>3</sup>P) + OH reaction is partly responsible. The lowest temperature at which a rate coefficient has been measured is 158 K, much higher than the temperatures that prevail in dense interstellar clouds (10K - 50K). Chemical models use an extrapolation from this value down to low temperatures, however, this remains highly uncertain. It is therefore desirable to extend these rate coefficient measurements to lower temperatures.

A method of co-photolysis has been used to create both unstable species in the cold flow of a CRESU apparatus using the same VUV laser pulse. This has been achieved while ensuring that the O(<sup>3</sup>P) concentration is much greater than the OH concentration which allowed pseudo first-order kinetics be employed. The OH (v=0) concentration was monitored by off-resonance laser induced fluorescence. In this way rate coefficients for the O(<sup>3</sup>P) + OH reaction have been measured down to 39K, the results and significance of which are presented.

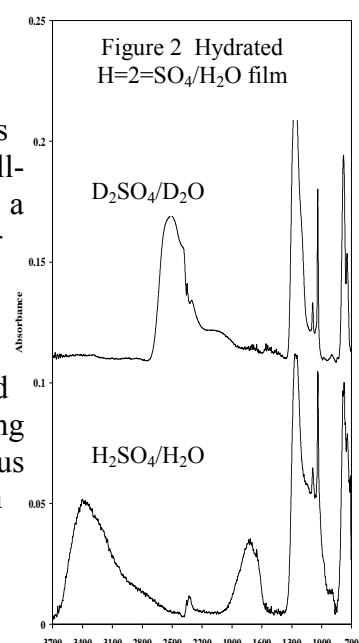
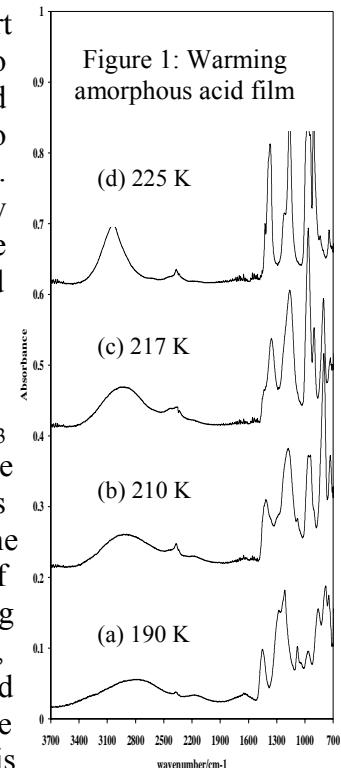
# Experimental Identification of New Low Temperature Hydrates of Sulfuric Acid

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The interaction of  $\text{SO}_3$  and  $\text{H}_2\text{O}$  at low temperatures upon an inert surface has been studied with infrared spectroscopy and compared to the predictions of recent computational studies. By controlled variation of temperature and reaction conditions, various low-ratio  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  species have been condensed and characterized. Amorphous mixtures of sulfuric acid and water can be formed at low temperatures under conditions of low water availability. These deposits show a vibrational spectrum very similar to that observed for  $\text{H}_2\text{SO}_4$  in dilute inert gas matrices (Fig 1a). That anhydrous  $\text{H}_2\text{SO}_4$  cannot be formed under these conditions (*i.e.* water is always present in the condensed film) supports gas phase experimental and theoretical observations that the reaction of  $\text{SO}_3$  with  $\text{H}_2\text{O}$  requires at least two  $\text{H}_2\text{O}$  molecules, even when the reaction occurs heterogeneously. Upon heating, this amorphous sulfuric acid/water mixture evolves the excess water trapped in the film and transforms first into an ordered 1:1 molecular complex of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  (Fig 1b) and then into molecular sulfuric acid (Fig 1c). The 1:1 complex is characterized by  $\text{H}_2\text{SO}_4$  vibrations which, although lower in frequency than those for the initially formed amorphous acid/water mixture, are clearly different from those observed for condensed anhydrous  $\text{H}_2\text{SO}_4$ . Additionally, this complex is characterized by a readily identifiable vibration of the coordinated  $\text{H}_2\text{O}$  molecule. The vibrational spectroscopic observation of such a complex provides further evidence in support of the conclusions of microwave and theoretical studies that such a complex is stable at low temperatures in clusters.

The addition of water to the amorphous  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  mixture results in the formation of a new material with a reproducible and well-defined vibrational spectrum (Fig 2). Through the use of a combination of literature theoretical predictions, thermal behavior and spectroscopic arguments, this material is identified as a stable higher ratio molecular  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  complex with a probable structure of  $\text{poly}(\text{H}_2\text{SO}_4(\text{H}_2\text{O})_2)$ . Given additional energy, this material irreversibly transforms into an ionised sulfuric acid hydrate, namely the monohydrate  $\text{H}_3\text{O}^+\text{HSO}_4^-$ . Further heating produces the anhydrous molecular acid as seen in previous experiments. This study presents the first experiment observation of this un-ionized complex.



There are atmospheric implications as a result of the stability of these compounds. Since the majority of atmospheric sulfate aerosol are thought to be formed from both the gaseous nucleation of  $\text{SO}_3$  and water and through the heterogeneous hydration of  $\text{SO}_3$  on water droplets, it is likely that these species are involved directly in the process of aerosol formation, although it is unlikely that they are long-lived in the bulk aerosol under typical ambient conditions. However, the reproducibility and stability of formation of these materials gives experimental credibility to the suggestion that un-ionized acid hydrates may be important surface species on aerosols, since these molecular species are potentially far more stable at the aerosol/vacuum interface than any ionic species.

Fiacco, D.L.; Hunt, S.W.; Leopold, K.R. *J. Am. Chem. Soc.* 2002, 124, 4504.

Bandy, A.R.; Ianni, J.C. *J. Phys. Chem. A.*, 1998, 102, 6533.

Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A.*, 1999, 103, 3535.

Horn A.B.; Sully, K.J., *J. Chem. Soc.: Faraday Trans.* 1997, 93, 2741.

Couling SB; Sully KJ; Horn AB (2002). Submitted to *J. Am. Chem. Soc.*

# **Polarisation Spectroscopy: A Novel Technique for the Study of Collisional Energy Transfer**

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Previous work in this group has investigated collisional energy transfer (ET) using laser-induced fluorescence (LIF). Polarisation spectroscopy (PS) is an established spectroscopic technique but is relatively unexploited in the field of collisional ET. A circularly or linearly polarised pump beam creates anisotropy amongst the magnetic sublevels within a sample. A crossed polariser initially blocks a weak, linearly polarised probe beam. It is modified by the pumped sample and the PS signal is the fraction newly transmitted through the crossed polariser.

A PS experiment has been established to investigate collisions of the OH radical. This is a species important in combustion and the atmosphere. Preliminary studies have verified the principles of the technique, achieving a high level of signal-to-noise. Future work will investigate the polarisation state of population that has been collisionally transferred.

# Excited State Dynamics of Toluene – Rare Gas van der Waals Clusters

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Laser induced fluorescence methods have been employed to study the dynamics of electronically excited van der Waals clusters of toluene with rare gas atoms in a supersonic expansion. In particular, the fluorescence excitation spectra have been recorded in the region of the  $S_1$ — $S_0$  transition.

The fluorescence lifetimes of the excited complexes are shown to depend strongly both on the vibronic level excited and on the cluster partner. The external heavy atom effect is very clearly demonstrated in the origin band ( $\tau = 80$  ns, 42 ns and  $< 10$  ns for toluene, Ar — toluene and Kr — toluene respectively); the cluster partner enhancing the rate of intersystem crossing through spin-orbit induced coupling of  $S_1$  and  $T_2$ . Excitation of higher vibrational levels leads to more complicated fluorescence decay profiles reflecting the vibrational predissociation of the complexes and the subsequent fluorescence of electronically excited toluene monomers.

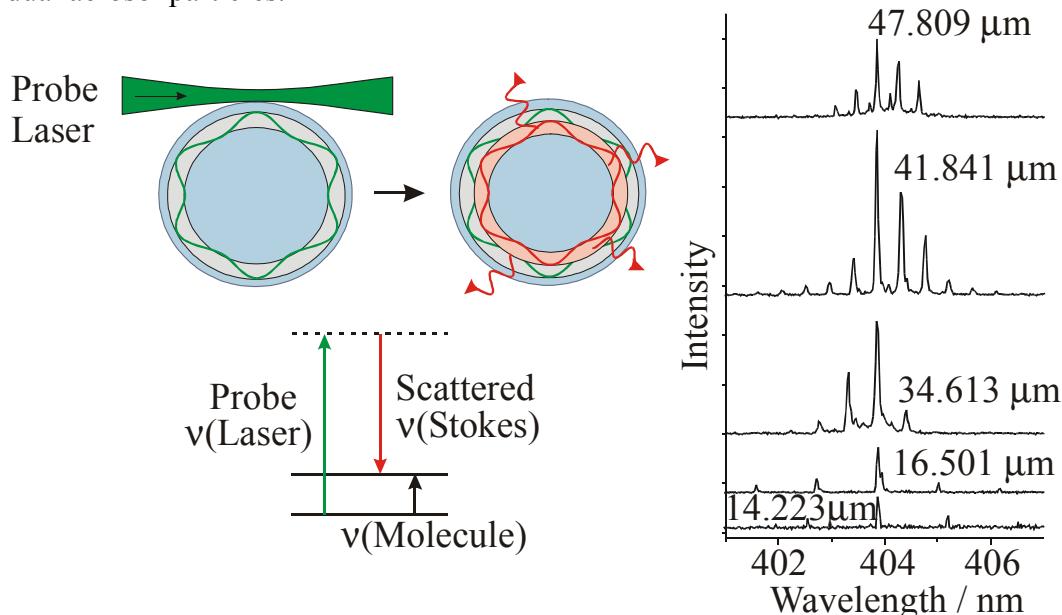
# Analysis of Heterogeneous Aerosol Particles using Cavity Enhanced Raman Spectroscopy

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Cavity Enhanced Raman Spectroscopy (CERS) is a relatively new technique developed by members of the optical physics community. The technique enables the size, morphology, refractive index, temperature and chemical composition of spherical cavities, such as aerosol droplets, to be probed. The technique relies on cavity modes or 'Whispering gallerys', which are akin to the trapping of sound waves by the whispering gallery of St Paul's cathedral in London. Light of a given discrete wavelength can be trapped within a spherical particle and undergo almost complete total internal reflection. This total internal reflection results in the light travelling several meters within a particle of micron diameter. This provides us with the possibility of a greatly increased sensitivity to a variety of spectroscopic techniques including Raman scattering. Light that has entered a whispering gallery mode leads to Raman scattering from molecules within the particle. Discrete wavelengths within the Raman band can then become trapped within whispering gallery modes and stimulate further molecules to Raman scatter light at the same wavelength, providing a massively enhanced Raman signal.

Here we provide preliminary results using this technique on a variety of water based aerosol droplets. We can acquire a spectroscopic fingerprint of a single aerosol particle with a single laser shot. The CERS fingerprint permits the accurate determination of the droplet size and refractive index, and this is illustrated in the figure for droplets with a radii of 14 to 50  $\mu\text{m}$ . The presence of further Raman bands from other constituents can permit the direct identification of the droplet composition. Ongoing work is attempting to develop this as a quantitative method for determining droplet composition. This technique will hopefully provide a tool for the non-destructive analysis of individual aerosol particles *in situ*, providing a variety of information from size distribution to depth profiling and chemical composition of individual aerosol particles.



# Quantum Scattering on Coupled *ab initio* Potential Energy Surfaces: A Study of Spin-Orbit Effects in the $\text{Cl}(^2\text{P}) + \text{HCl} \rightarrow \text{ClH} + \text{Cl}(^2\text{P})$ Reaction

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We present the results of accurate quantum dynamical calculations for the  $\text{Cl}(^2\text{P}) + \text{HCl} + \text{Cl}(^2\text{P})$  reaction. The calculations have been performed employing a coupled channel reactive scattering method based on hyper-spherical coordinates.<sup>1,2</sup> We included the three potential energy surfaces<sup>3</sup> ( $1^2\text{A}'$ ,  $2^2\text{A}'$  and  $1^2\text{A}''$ ) that correlate to the ground state of the reactants and products and also the electrostatic, Coriolis and spin-orbit couplings.

The spin-orbit coupling has been included using a spin-orbit parameter,  $\lambda$ , that is assumed to be independent of nuclear geometry.<sup>2</sup> We studied the influence of the magnitude and sign of  $\lambda$  on the reaction dynamics. We have performed calculations for values of  $\lambda$  ranging from 0 to  $\pm 100\%$  of the true Cl atom value ( $\lambda_{\text{Cl}} = -588 \text{ cm}^{-1}$  or  $-0.073 \text{ eV}$ ,  $\lambda = s\lambda_{\text{Cl}}$  with  $-1 \leq s \leq 1$ ) to determine how the dynamics change with  $\lambda$ .

We present spin-orbit state resolved cumulative reaction probabilities and show how they change with the variations of  $\lambda$ . The cumulative reaction probabilities show some broad resonance-like features. In order to determine which of these resonances can be associated with the coupled multi-surface nature of the dynamics, we also present cumulative reaction probabilities obtained in calculations where the coupling potential is set to zero.

- [1] T. W. J. Whiteley, A. J. Dobbyn, J. N. L. Connor and G. C. Schatz, *Phys. Chem. Chem. Phys.* **2**, 549 (2000).
- [2] G. C. Schatz, P. McCabe and J. N. L. Connor, *Faraday Discuss.* **110**, 139 (1998).
- [3] A. J. Dobbyn, J. N. L. Connor, N. A. Besley, P. J. Knowles and G. C. Schatz, *Phys. Chem. Chem. Phys.* **1**, 957 (1999).

# FTIR Emission Studies of Reactions of Small Hydrocarbon Radicals

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The Time-Resolved Fourier Transform Infrared (TR-FTIR) emission technique has been applied to the study of reactions of the lowest singlet and ground triplet states of methylene ( $^1\text{CH}_2$  and  $^3\text{CH}_2$ ) and  $\text{CH}_3$ . Radicals were generated by laser photolysis of a suitable precursor in a Welsh Cell and TR-FTIR emission spectra were obtained using a commercial interferometer (Bruker IFS/66), operated in step-scan mode.

$^1\text{CH}_2$  and  $^3\text{CH}_2$  were generated by photolysis of  $\text{CH}_2\text{CO}$  at 308 nm and 351 nm. At 308 nm, emission bands from vibrationally excited CO,  $\text{C}_2\text{H}_4$  and  $\text{CH}_2\text{CO}$  were observed, consistent with reaction of  $^1\text{CH}_2$  with the precursor and energy transfer from CO to  $\text{CH}_2\text{CO}$ . At 351 nm, there is insufficient energy to form vibrationally excited CO and the reaction of  $^3\text{CH}_2$  with  $\text{CH}_2\text{CO}$  is very slow ( $k < 2 \times 10^{-15} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ). However there is emission from highly vibrationally excited  $\text{CH}_2\text{CO}$ , arising from internal conversion from the first excited singlet state to the ground state, followed by vibrational cascade.

In the presence of  $\text{O}_2$ , additional emission was observed, and assigned to CO,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ , which are expected products of reaction of both  $^1\text{CH}_2$  and  $^3\text{CH}_2$ . The kinetics of the  $\text{O}_2 + \text{CH}_2$  reaction have been studied by analysis of the  $\text{H}_2\text{CO}$  emission. At 351 nm the rate constant for the formation of  $\text{H}_2\text{CO}$  agrees with that for the removal of  $^3\text{CH}_2$  by  $\text{O}_2$  from previous studies. At 308 nm, the rate of  $\text{H}_2\text{CO}$  production is faster, suggesting that the  $^1\text{CH}_2 + \text{O}_2$  reaction is direct, and does not proceed via quenching to  $^3\text{CH}_2$ .

$\text{CH}_3$  radicals were produced from 193 nm photolysis of acetone. Along with the  $\text{CH}_3 \Delta v_3 = -1$  band at  $3100 \text{ cm}^{-1}$ , there is also an emission band centred at  $2900 \text{ cm}^{-1}$  assigned to  $\text{C}_2\text{H}_6$  formed by recombination of  $\text{CH}_3$  radicals. Interestingly, the spectral distribution of this band remains approximately constant with time, and the emission is not vibrationally absorbed by a cold gas filter of ground state ethane. Rate measurements, made as a function of pressure of acetone, indicate that slow recombination of  $\text{CH}_3$  radicals is followed by fast vibrational relaxation, and that emission observed is from highly excited  $\text{C}_2\text{H}_6$  products.

# Low-Temperature Kinetics of Reactions of OH and C<sub>2</sub>H

## Using a Pulsed Laval Nozzle Apparatus

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The kinetics of reactions of the OH and C<sub>2</sub>H radical have been studied at low temperatures using the environment of a pulsed Laval nozzle supersonic expansion. Following production via the laser flash-photolysis of a suitable precursor, the time-profile of the OH radical was monitored using laser-induced fluorescence (LIF) in the (1,0) band of the A<sup>2</sup>Σ<sup>+</sup> - XΠ<sub>i</sub> transition at 282 nm, whereas the C<sub>2</sub>H radical profile was monitored using chemiluminescence at 430 nm from CH(A<sup>2</sup>Δ) following the reaction between C<sub>2</sub>H and O<sub>2</sub>. The gas number density and temperature distribution in the expansion were thoroughly characterised using dynamic pressure measurements and LIF spectroscopy of OH [1]. Rate coefficients at T = 103 K were determined for the reactions of OH with propene and 1-butene [1], and for the reactions of C<sub>2</sub>H with acetylene, O<sub>2</sub>, methylacetylene, allene, ethene, propene and 1-butene [2,3]. Measurements of the rate coefficients at room temperature and comparison with previous data suggest a negative temperature dependence for all reactions. For the reactions of C<sub>2</sub>H with methylacetene and allene the results at 103 K are in good agreement with measurements performed in a continuous Laval expansion of a CRESU apparatus [4].

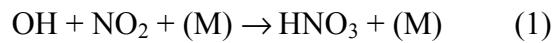
- [1] A. B. Vakhtin, S. Lee, D. E. Heard, I. W. M. Smith and S. R. Leone, "Low-temperature kinetics of reactions of OH radical with propene and 1-butene studied by a pulsed Laval nozzle apparatus combined with laser-induced fluorescence", *J. Phys. Chem. A*, **105**, 7889-7895 (2001).
- [2] A. B. Vakhtin, D. E. Heard, I. W. M. Smith and S. R. Leone, "Kinetics of reactions of C<sub>2</sub>H radical with O<sub>2</sub>, acetylene, methylacetylene and allene studied by a pulsed laval nozzle apparatus at T = 103 K", *Chem. Phys. Lett.*, **344**, 317-324 (2001).
- [3] A. B. Vakhtin, D. E. Heard, I. W. M. Smith and S. R. Leone, "Kinetics of C<sub>2</sub>H radical reactions with ethene, propene and 1-butene measured in a pulsed Laval nozzle apparatus at T = 103 K and 296K", *Chem. Phys. Lett.*, **348**, 21-26 (2001).
- [4] D. Carty, V. Le Page, I. R. Sims and I. W. M. Smith, *Chem. Phys. Lett.*, **344**, 310 (2001).

# Recombination Kinetics of Thermal and vibrationally excited OH with NO<sub>2</sub> and NO

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The three-body recombinations of OH with NO<sub>x</sub> are important in both tropospheric and stratospheric chemistry.



In this work we report recent measurements of the rate coefficients for the recombination reactions of the OH radical with NO<sub>2</sub> and NO. Measurements with thermal OH were made under realistic atmospheric conditions using the Pulsed Laser Photolysis - Pulsed Laser Induced Fluorescence technique. Vibrational deactivation measurements were made as a route to the high pressure limiting rate. We have recently reported measurements on the rate coefficients for the thermal reaction (1) in air, N<sub>2</sub>, O<sub>2</sub> and He buffer gases at room temperature and as a function of pressure (30-700 Torr), together with measurements in N<sub>2</sub> at 273 K. We obtain values for the deactivation of vibrationally excited OH of  $v=1,2,3,4$ , and 5:  $(6.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We will also report data for reaction (2) as a function of pressure (30-700 Torr) in N<sub>2</sub>, and (30-900 Torr) in Helium at room temperature. One of the goals of this work is to evaluate the use of vibrational deactivation as a route to the high pressure limiting rate with a conventional fall off analysis of thermal rate data for this complex reaction system. This work was supported by the National Science Foundation.

# Vibrational Activation of O( $^3P$ ) Abstraction Reactions

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The reaction  $O(^3P) + CH_4 \rightarrow OH + CH_3$  exhibits a significant activation barrier. Theoretical studies of the reaction have predicted a substantial enhancement of reactivity due to the vibrational excitation of the  $CH_4$  reactant.

The work presented represents an experimental study on the effect of selectively exciting the  $CH_4$  by IR pumping. The study also includes measurements on the closely related system  $O(^3P) + HCl \rightarrow OH + Cl$ , which is known experimentally to be substantially enhanced.

The principle observation is that IR pumping of  $CH_4$  does not produce any enhanced OH production from the  $O(^3P) + CH_4$  reaction above the level of our limiting signal-to-noise. This is in contrast to  $O(^3P) + HCl$  where we readily observe that overtone pumping of HCl produces substantially increased production of OH.

# Chemical Composition of Individual Particles Detected at Eskdalemuir, Scotland – Correlations Between Ions Observed in Fine and Coarse Particles

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Mathew R. Heal<sup>1</sup>, Martin D. King<sup>3</sup>, Robert Kinnersley<sup>2</sup>,  
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An aerosol time-of-flight mass spectrometer (ATOFMS) was used to determine, in real time, the size and chemical composition of individual particles in atmospheric air at the remote site of Eskdalemuir, Dumfries and Galloway, Scotland. Sampling began at 20:00 on day 176 of 2001 (25/06/01) and continued until 09:00 on day 181 of 2001. In all 51980 individual particles were analysed. Back trajectories, calculated using British Atmospheric Data Centre models, reveal that two distinct air masses were encountered, a polluted air mass that passed over the British mainland before reaching Eskdalemuir and a cleaner air mass that originated from the Arctic and journeyed over the Atlantic.

The results have been analysed to determine correlations between various chemical species in both fine and coarse particles, and thus help elucidate the sources of the particulate matter.

# Experimental and Theoretical Study of Intramultiplet Transitions in Collisions of Si( ${}^3P_j$ ) and C( ${}^3P_j$ ) with He

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Collision-induced fine structure transitions in atoms have been the subject of many experimental and theoretical studies because of their interest in both physical and chemical processes involved in different fields such as chemical lasers, combustion, atmospheric and interstellar chemistry. From a chemical point of view, collisionally induced intramultiplet mixing are considered as a benchmark for understanding fine structure effects in chemical reactions. Rates of excitation of fine structure transitions of abundant atoms, like carbon or oxygen, by collisions with helium or hydrogen are also valuable sources of information on conditions in interstellar clouds, where the temperature can be as low as 10 K. For instance the relative population of neutral carbon atoms in excited fine-structure levels of the ground state is used to probe the density and the temperature in diffuse HI regions. Abundant ground state atoms, especially C and O, also play an important role in cooling interstellar clouds because their collisional excitation by H<sub>2</sub>, H, or He to an excited fine structure level can be followed by radiative deexcitation.

On this poster, we present an experimental and a theoretical study of intramultiplet relaxation of Si( ${}^3P_j$ ) and C( ${}^3P_j$ ) by collisions with helium at temperatures down to 10 K. The experimental work was achieved using the CRESU facilities of Rennes and Birmingham. Silicon and carbon atoms were generated by 266 nm laser photolysis of Si(CH<sub>3</sub>)<sub>4</sub> and C<sub>3</sub>O<sub>2</sub> respectively. For both systems (Si + He and C + He), kinetic evolutions of the atomic spin-orbit populations were directly monitored using resonant ultraviolet (for silicon) or vacuum-ultraviolet (for carbon) laser induced fluorescence. The spin-orbit excitation and relaxation rate constants were then deduced over the temperature range 15-49 K for Si( ${}^3P_j$ ) + He and at 15 K for C( ${}^3P_j$ ) + He. Three sets of interaction potentials have been generated for the  ${}^3\Sigma^-$  and  ${}^3\Pi$  electronic states of Si-He and C-He systems. Quantum-mechanical calculations have been performed on these potential curves for the spin-orbit relaxation and excitation. Cross sections and rate constants for both intramultiplet relaxation collisions were then deduced over a wide range of temperatures (from 10 to 500 K). These results are very sensitive to the interaction potentials. For Si( ${}^3P$ ) + He system an overall good agreement between the theoretical and experimental rate constants is found, while for the C( ${}^3P$ ) + He system the theoretical rate constants is found to be bigger than the experimental ones.

# Steric Effects in the Photodissociation Dynamics of Fully Size- and Quantum State-Selected van der Waals Complexes

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High-resolution IR-UV-UV multiple resonance techniques are employed to elucidate photodissociation dynamics within quantum state-selected Ar-HOD and Ar-H<sub>2</sub>O van der Waals clusters. A Fourier transform linewidth limited optical parametric oscillator operating in the region of the OH second overtone is used to prepare individual rovibrational states which are then selectively photodissociated at specific excimer wavelengths. Fluorescence excitation of the resulting OH (OD) fragments yields dynamical information on the photofragmentation event and resulting intra-cluster collisions.

This strategy is used to characterize spectroscopically the  $\Pi(1_{01})$ ,  $v_{\text{OH}} = 3 \leftarrow \Sigma(0_{00})$ ,  $v_{\text{OH}} = 0$  overtone band of the Ar-HOD complex with origin at 10648.27 cm<sup>-1</sup>. The effects of clustering on the dissociation dynamics are inferred by comparison of the OD photofragment quantum state distributions resulting from dissociation of single rovibrational states of the complex with those from isolated HOD photodissociation.

The initial internal state of the complex is shown to play a vital role in the dissociation dynamics: Comparison of the current Ar-HOD  $\Pi(1_{01})$ ,  $v_{\text{OH}} = 3$  results with previously published results for the Ar-H<sub>2</sub>O  $\Sigma(0_{00}) |03\rangle$  state reveal dramatic differences in the photofragment quantum state distributions. The contrasting dynamics of the two systems are interpreted as a beautiful manifestation of the nodal structure of the vibrational state in the parent complex and the way in which it governs the collision probability between the Ar atom and the escaping photofragments.

# The Kinetics of OH + H<sub>2</sub>O<sub>2</sub> at Cryogenic Temperatures

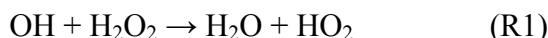
Andrei Vakhtin<sup>1</sup>, David C. McCabe<sup>2,3</sup>, A. R. Ravishankara<sup>2,3</sup>,  
and Stephen R. Leone<sup>1,3</sup>

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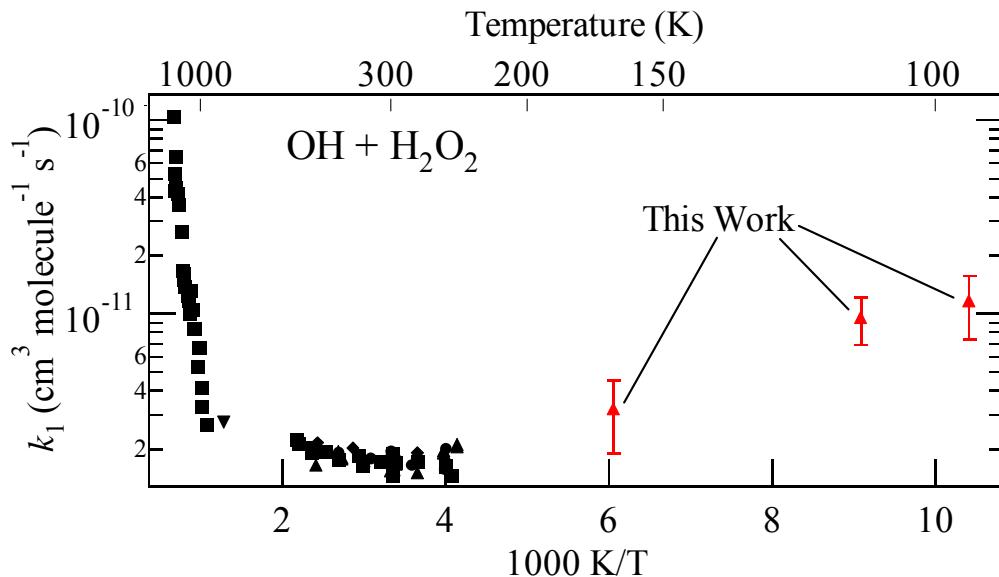
The reaction of OH with hydrogen peroxide, R1,



is of importance in the upper troposphere and stratosphere. R1, following H<sub>2</sub>O<sub>2</sub> formation by HO<sub>2</sub> self-reaction, is a HO<sub>x</sub> sink (HO<sub>x</sub>  $\equiv$  OH + HO<sub>2</sub>). The rate coefficient for this reaction,  $k_1$ , is difficult to measure below room temperature due to the low vapor pressure of H<sub>2</sub>O<sub>2</sub>; accordingly, published measurements of  $k_1$  vary by up to 30% at 250 K. However, accurate values of  $k_1$  are needed at this and lower temperatures ( $> 200$  K) for atmospheric purposes.

We have measured  $k_1$  at three temperatures from 96 – 165 K using a Laval nozzle expansion to achieve low temperature. Pulsed photolysis of the H<sub>2</sub>O<sub>2</sub> was used to produce OH; pulsed laser-induced fluorescence was used to detect the OH.

The rate coefficient becomes significantly larger at these temperatures, rising from  $1.7 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K to  $1.16 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 96 K. The negative temperature dependence of the rate coefficient below room temperature suggests that the reaction proceeds *via* a bound OH·H<sub>2</sub>O<sub>2</sub> intermediate. This data also suggests that extrapolating the positive temperature dependence that  $k_1$  displays at higher temperatures may underestimate the rate coefficient under upper tropospheric and lower stratospheric conditions.



Arrhenius plot of measured rate coefficients for OH + H<sub>2</sub>O<sub>2</sub>

# Rates of Formation of Ozone Isotopomers: A Theoretical Interpretation

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It is found that the relative probabilities for the  $0 \rightarrow 1$  vibrational excitation in collisions of oxygen isotope  $^a\text{O}$  atom approaching  $^b\text{O}^c\text{O}$  molecule along a path which has essentially the same geometry as the ozone dissociation path in the asymptotic region coincide quite well with the observed relative formation rates of the  $^a\text{O}^b\text{O}^c\text{O}$  isotopomers formed in  $^a\text{O} + ^b\text{O}^c\text{O}$  collisions. It may thus be concluded that isotope selectivity in ozone formation arises primarily from the transfer of the excess kinetic energy of the relative motion into the  $\text{O}_2$  vibration which produces a vibrationally excited  $\text{O}_3^*$  and not from the subsequent collisional deactivation and stabilization through the bath gas. This is in accord with the conclusions arrived at in the recent experimental studies of third-body dependence of ozone formation rates. Further arguments about third-body effects are presented in support of the model.

# Dynamics of the Reactions of $\text{Cl}({}^2\text{P}_{3/2})$ with $\text{CH}_3\text{NH}_2$ and its Deuterated Isotopomers

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The dynamics of the hydrogen abstraction reactions of  $\text{Cl}({}^2\text{P}_{3/2})$  with  $\text{CH}_3\text{NH}_2$ ,  $\text{CD}_3\text{NH}_2$ ,  $\text{CH}_3\text{ND}_2$ , and  $\text{CD}_3\text{ND}_2$  have been examined experimentally and theoretically. Ground spin-orbit state  $\text{Cl}({}^2\text{P}_{3/2})$  atoms were produced with a monoenergetic speed distribution by photolysis of  $\text{Cl}_2$  at 355 nm, resulting in collision energies of  $5.5 - 6.0 \pm 1.2 \text{ kcal mol}^{-1}$ . The nascent quantum state distributions of the  $\text{HCl}(v' = 0, J')$  and/or  $\text{DCl}(v' = 0, J')$  reaction products were measured by resonance-enhanced multiphoton ionisation spectroscopy in a time-of-flight mass spectrometer. The  $\text{HCl}(v' = 0, J')$  distribution produced in the reaction of the non-deuterated amine can, in principle, be a composite of distributions from the two abstraction channels. Preliminary analysis of the  $\text{HCl}$  distributions observed from the reaction of the partially deuterated amines allows separation of the two components, showing a broad, although not statistical, distribution for abstraction from C and a colder distribution for abstraction from N.  $\text{DCl}(v' = 0, J')$  product state distributions also show this behaviour, with a similar fraction of the available energy being deposited in rotation.

Complementary *ab initio* calculations were performed to elucidate the mechanisms of hydrogen abstraction in these systems. Optimised geometries and zero-point vibrational frequencies of molecular complexes and transition states along the reaction pathway were calculated at the MP2/6-311G(d,p) level, with further single-point energy refinement carried out at the G2//MP2/6-311G(d,p) level. Agreement between the *ab initio* energetics and experimental data is good. A near collinear  $\text{Cl}\cdots\text{H}\cdots\text{C}$  transition state geometry is found, while the  $\text{Cl}\cdots\text{H}\cdots\text{N}$  transition state is significantly bent, suggesting that impulsive release is not responsible for the rotational distributions observed experimentally. Comparisons will be drawn with previous experimental and theoretical results obtained for the hydrogen abstraction reactions of  $\text{Cl}({}^2\text{P}_{3/2})$  with alcohols and ethers.

# Laboratory Experiments on the Atmospheric Fate of $\text{CF}_3\text{CXY}$ Radicals

Rouslan V. Olkhov<sup>\*</sup> and Ian W.M. Smith

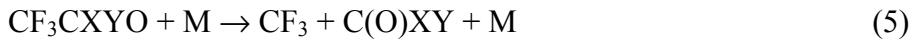
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Negative ecological reputation of chlorofluorocarbons (CFC) released into atmosphere resulted in an international effort to replace them with substitute compounds, which would be more environmentally friendly. Hydrofluorocarbons (HFC) are thought as good candidates since the presence of a hydrogen atom allows initiation of their decomposition in troposphere by reaction with OH radical, which leads to much shorter atmospheric lifetimes of HFCs compare to those of CFCs.

The atmospheric degradation of hydrofluorocarbons  $\text{CF}_3\text{CXYH}$  (X,Y = F or H) begins according the following reaction scheme:



If Y = H, the alkoxy radicals produced in reaction 4 may undergo further H-abstraction reaction with oxygen to produce or decompose:



The time resolved IR absorption technique was used to study kinetics of reactions 3 and 5. The fluorinated ethyl iodides  $\text{CF}_3\text{CF}_2\text{I}$ ,  $\text{CF}_3\text{CH}_2\text{I}$  and  $\text{CF}_3\text{CFHI}$  served as precursors to produce corresponding alkyl radicals upon photolysis at 248 nm. Products of  $\text{CF}_3\text{CXY}$  degradation in gas mixtures containing  $\text{O}_2$  and  $\text{NO}$  at 30 Torr and in the temperature range 198-298 K were monitored in time via absorption of IR laser diode radiation. The results obtained are discussed.

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# Interrogation of Plasmas Using Diode Lasers

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Diode laser absorption spectroscopy has been used to probe the 2p10 excited state of argon (which lies 12.91 eV above the ground state) via a transition at 687.129 nm in a low pressure inductively coupled plasma. Multiple harmonic wavelength modulation spectroscopy has been used for sensitivity enhancement. Variations in the temperature of the plasma have been recorded as a function of discharge power by fitting the absorption signals and extracting the Doppler widths of the absorption lines. The translational temperature under the plasma chamber conditions is considerably higher than ambient temperature. This could reflect the increased importance of ion-neutral collisions in the plasma.

Cavity enhanced diode laser absorption spectroscopy is explained in terms of the cavity transmission function for a rapidly swept coherent source. The sensitivity of the technique is demonstrated on forbidden oxygen transitions (the (1,0) band of the  $b^1\Sigma_g^+ - X^3\Sigma_g^-$  transition) and on low concentrations of the metastable A-state of N<sub>2</sub> in a plasma chamber. Once again the gas temperature in the plasma chamber is derived from the data. In this case both the kinetic temperature and the rotational temperature of N<sub>2</sub> have been extracted, as a function of plasma chamber power, and are found to be in good agreement.

# Imaging the Reactions of Molecular Dications: A New Probe of Dicationic Reaction Dynamics and Energetics.

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Small molecular doubly-charged ions (dications) are usually highly energy-rich and reactive metastable species. However, despite their high internal energy content, several molecular dications have recently been shown to display considerable chemical reactivity with neutral species. For example:



This poster displays the first results from a new coincidence experiment designed to study the dynamics of these dication reactions. In the new experiment a beam of ions is extracted from a home-built ion source and energy selected with a hemispherical energy analyser. The reactant dications of interest, e.g.  $\text{CF}_2^{2+}$ , are selected from the ion beam and collide in the source region of a time-of-flight mass spectrometer (TOFMS) with the neutral reactant and the reactions of interest occur. Following the interaction of the dication beam with the neutral target the ionic products are detected and analysed by pulsing on an extraction voltage (30-50 kHz) across the source region of the TOFMS. The ions are detected at a position sensitive detector interfaced to fast timing electronics. This position sensitive data can be interpreted to yield the initial velocity vectors of the two charged fragments from the bimolecular dication reaction. From these velocity vectors the dynamics of the reaction can be determined. Experiments can be carried out with either a pulsed ( $\sim 0.5 \mu\text{s}$ ) or continuous beam of reactant dications. The pulsed beam produces higher quality data at the expense of longer run times.

The results from commissioning experiments will be presented. These experiments have involved the study of simple (two-body) atomic electron transfer reactions:



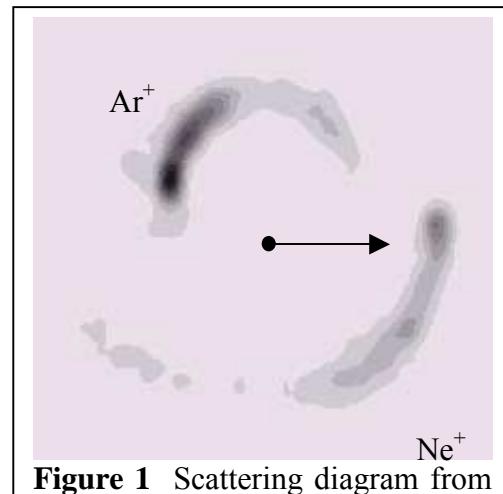
From the position sensitive data we can extract, as predicted, key quantities which characterise the dynamics of the reaction. For example:

- the angular distribution of each of the product ions
- the angle between the product ions as they separate
- the translational and internal energies of the product ions
- the scattering diagram
- the electronic states of the products and reactants from the energy balance.

The poster will also present the first results from the study of a bimolecular reaction producing three products:



where the real power of the coincident technique is apparent as, from the velocity vectors of the ionic products, we can derive the velocity of the neutral fragment using conservation laws.



**Figure 1** Scattering diagram from a PSCO spectrum of collisions of  $\text{Ne}^{2+}$  with Ar. The direction of the  $\text{Ne}^{2+}$  velocity is indicated by the arrow. The scattering centre is marked by a dot.

# Pressure Induced Line Shifts and Broadening of Atmospherically Important Species

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The pressure broadening coefficients for several transitions in the  $2v_5$  band of formaldehyde in the overtone region around  $1.76\mu\text{m}$  have been measured for a number of bath gases using cavity enhanced absorption spectroscopy (CEAS). The bath gases include He, Ne, Ar, Kr, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O; the self-broadening coefficient of formaldehyde has also been measured. These pressure broadening coefficients have been used to calculate inelastic collision cross-sections which are larger than those predicted from a simple hard sphere model. The data has also been used to construct Parmenter-Seaver plots of cross-section versus well-depth for each gas and extrapolated to obtain a well-depth for the formaldehyde dimer which is compared with theory.

A simple technique is demonstrated for the accurate determination of pressure induced line shifts of water in air. High and low pressure water samples are simultaneously probed on selected overtone transitions at  $1.32\mu\text{m}$  using a current modulated distributed feedback (DFB) diode laser and harmonic detection. Comparisons are made between first and second harmonic detection, and wavelength and frequency modulation regimes. The effect of modulation broadening on the returned line shifts is quantified.

# Experimental Observations and Quasiclassical Trajectory Calculations of the Reaction Dynamics of Cl Atoms with Methanol and Methane

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The dynamics of the ground state  $\text{Cl}({}^2\text{P}_{3/2})$  atom reaction with methanol have been studied both experimentally and theoretically.<sup>1</sup> The reaction was photoinitiated by 355 nm photolysis of  $\text{Cl}_2$  to produce monoenergetic  $\text{Cl}({}^2\text{P}_{3/2})$  atoms that react with ground state methanol under single collision conditions. The rotational ground state population distribution of the nascent  $\text{HCl}(v'=0)$  products was probed by 2+1 resonance-enhanced multiphoton ionization in a time-of-flight mass spectrometer. Nascent  $\text{HCl}(v'=0)$  products from this reaction at a mean collision energy of 5.60 kcal/mol (1960  $\text{cm}^{-1}$ ) exhibit a rotational population distribution that peaks at  $J'=3 - 5$ , i.e. significantly hotter than  $\text{HCl}(v'=0)$  products from Cl atom reaction with ground state methane, which peak at  $J'=0$ .<sup>2</sup>

*Ab initio* calculations were performed in order to examine the mechanism of Cl atom abstraction of hydrogen from methanol and methane. Optimized geometrical structures and vibrational frequencies of molecular complexes and transition states on the reaction pathway were obtained at the MP2/6-311G(d,p) level and their energies were further refined at the G2 level of theory. Comparisons are drawn between mechanisms and energetic pathways of these reactions. The greater degree of rotational excitation of the HCl for abstraction of an H atom from methanol compared to methane is attributed to an attractive dipole-dipole interaction between the polar HCl and  $\text{CH}_2\text{OH}$  fragments, which causes a well in the products region on the potential energy surface (PES).

To test our hypothesis we have carried out a preliminary study of the post-transition state dynamics of both reactions by propagating classical trajectories using a velocity Verlet algorithm on an *ab initio* PES computed 'on the fly' at the MP2/6-311G(d,p) level. Reaction trajectories were initiated at the configuration of the transition state for both systems, with a small velocity directed along the reaction coordinate towards the product side. No energy was put into the transverse degrees of freedom. These initial conditions correspond to an overall angular momentum of roughly zero. The final classical angular momentum for HCl was found to correspond to  $J'=2.8$  and  $J'=0.0$  for methanol and methane reactions, respectively.

- [1] S. Rudić, C. Murray, D. Ascenzi, H. Anderson, J.N. Harvey and A.J. Orr-Ewing, *J. Chem. Phys.* 117, (2002), in press.
- [2] W.R. Simpson, T.P. Rakitzis, S.A. Kandel, T. Lev-On and R.N. Zare, *J. Phys. Chem.* 100, 7938 (1996).

# Aerosol Science: Studying the Fundamentals of Uptake

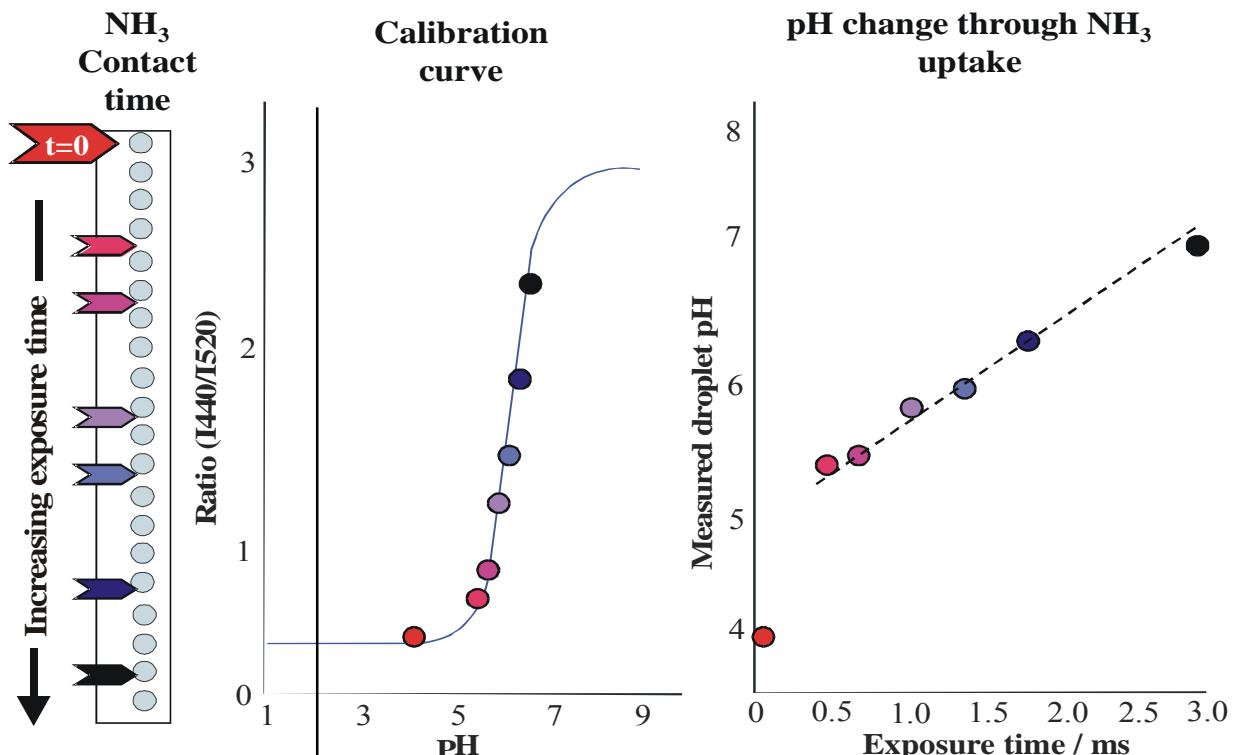
Robert M. Sayer, Robert D.B. Gatherer and Jonathan P. Reid

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Aerosol particles are known to play a significant role in the atmosphere through radiative effects, chemical speciation and reaction through uptake. We are currently developing a laser based technique that can provide insights into the fundamental processes occurring during the uptake of atmospherically relevant gases.

By doping droplets with a pH sensitive fluorescent dye, sensitive and accurate studies can be performed on species uptake. The fluorescence profile provides an indication of the pH achieved upon uptake of an acid or alkali gas. Preliminary work is focussing on the uptake of ammonia on water droplets. Initially we have been performing multiple droplet studies before moving towards single droplet studies. It is hoped to spatially depth profile the droplet pH from the droplet interface into the droplet bulk during the uptake process using the technique of cavity enhanced spectroscopy.

## Test Experiments on the Uptake of Ammonia onto Acidified Liquid Droplets



# Bond Selective Molecular Manipulation at Room Temperature with the STM: Desorption and Dissociation of Chlorobenzene on Si(111)-(7x7)

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We demonstrate bond selective atomic manipulation at room temperature with the STM in the chemisorbed system, chlorobenzene on Si(111)-(7x7). The molecule is chosen to present a "target" group, the C-Cl functionality and also have a "binding" group, the benzene ring which enables the room temperature dissociation of the C-Cl bond.

At surface bias voltages, +1V +2V +3V, chemisorbed chlorobenzene was detected on the surface. However, scanning at bias voltages higher than +3.5V induced dissociation of the C-Cl bond. The manipulation scans generate "half moon" features with the truncated edge always imaged before the rest of the "half moon". These features are attributed to chemisorbed Cl, liberated by the dissociation of the C-Cl bond in the line scan prior to the appearance of the bright "half moon" features.

Repeated pulsing of the tip (-4V, 50ms) made it possible to change the state of the tip, such that chemisorbed chlorobenzene imaged as a bright (not dark) feature at +2V. Tips of this type led to desorption of the chlorobenzene, i.e. excitation of the molecule-surface bond rather than the C-Cl. The probability of desorption per electron as function of sample bias was measured. No desorption was found for positive bias voltages below +2V; above this bias voltage the probability rose sharply and was still rising at +4V bias. Desorption was also found at negative sample bias voltages lower than -1V. The desorption probability as a function of tunneling current was also measured, showing a linear dependence which indicates the desorption process is not dependent on chemical or electrical field effects but is consistent with a negative ion resonance intermediate<sup>1</sup>.

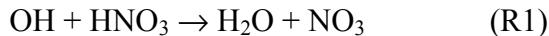
[1] G. P. Salam, M. Persson, R. E. Palmer, **49** (1994) 10 655

# The Reactions of OH (v = 1) and OD (v = 1) With HNO<sub>3</sub> and DNO<sub>3</sub>

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The reaction of OH with HNO<sub>3</sub> is of considerable interest because of its atmospheric importance and interesting kinetic behaviour.



The rate coefficient for reaction (1) is pressure dependent, increases with decreasing temperature, and shows unusual behaviour upon isotopic substitution. To further understand the mechanism of reaction (1), we have measured the rate coefficients for the removal of OH (v = 1) and OD (v = 1) by HNO<sub>3</sub> and DNO<sub>3</sub>. We used a pulsed photolysis, laser-induced fluorescence system with 248 nm photolysis of HNO<sub>3</sub> / DNO<sub>3</sub>, to produce vibrationally excited OH and OD.

These reactions are considerably faster than reaction (1) and its isotopic analogues:

Reaction	Rate coefficient at 296 K (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )
OH (v = 1) + HNO <sub>3</sub> → loss of OH (v = 1)	2.5 × 10 <sup>-11</sup> (R2)
OH (v = 1) + DNO <sub>3</sub> → loss of OH (v = 1)	5.8 × 10 <sup>-12</sup> (R3)
OD (v = 1) + HNO <sub>3</sub> → loss of OD (v = 1)	8.0 × 10 <sup>-12</sup> (R4)
OD (v = 1) + DNO <sub>3</sub> → loss of OD (v = 1)	1.7 × 10 <sup>-11</sup> (R5)

The above values for  $k_2$  and  $k_5$  agree well with previously published results [1]; to our knowledge there are no published measurements of  $k_3$  and  $k_4$ . These rate coefficients are 50 – 1200 times faster than the corresponding rate coefficients for the reactions of ground state OH / OD with HNO<sub>3</sub> / DNO<sub>3</sub>. Particularly in the case of  $k_3$  and  $k_4$ , where the fast rate coefficients cannot be explained by a resonant-energy transfer process, these large rate coefficients are probably due to the formation of an adduct of OH / OD and HNO<sub>3</sub> / DNO<sub>3</sub>. This adduct is likely to be structurally identical with the adduct involved in reaction (1), and the rate coefficients  $k_2$  –  $k_5$  are likely to be close to the rate coefficient for the formation of the OH•HNO<sub>3</sub> adduct from ground-state reactants [1]. Previous publications from our laboratory have estimated the rate coefficient for formation of this adduct by different means [2]; agreement between those estimates and the present measurements is satisfactory.

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We have estimated the yield of several trace photolysis products of  $\text{HNO}_3$  /  $\text{DNO}_3$  photolysis at 248 nm. Approximately 1% of the OH produced is in the ( $v = 1$ ) state; approximately 0.5% is in ( $v = 2$ ). OD yields in these states appear to be similar. Additionally, we see evidence that electronically excited  $\text{NO}_2$  is produced by  $\text{HNO}_3$  /  $\text{DNO}_3$  photolysis at this wavelength.

The temperature dependence of  $k_2 - k_5$  has also been measured; each reaction shows an effective activation energy ( $E_a / R$ ) of  $\sim -600$  K. This unusual negative temperature dependence, and the implications of these measurements for the mechanism of the ground-state reaction (1), will be discussed.

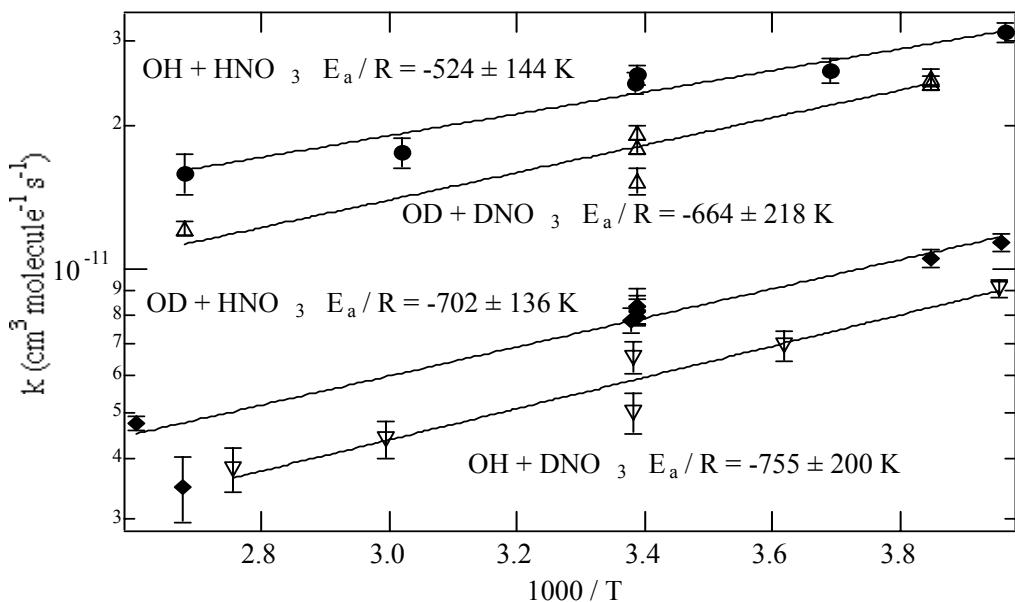


Figure 1. Arrhenius plot of rate coefficients  $k_2 - k_5$  with effective activation energies.

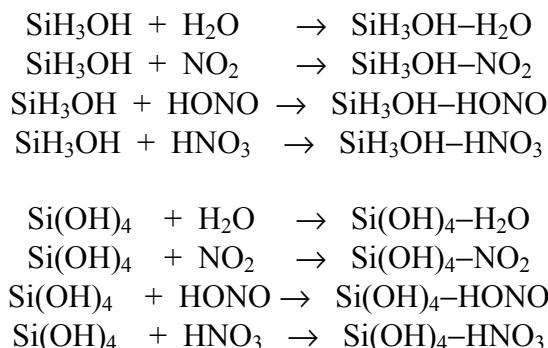
- [1] I. W. M. Smith and M. D. Williams, *J. Chem. Soc. Faraday Trans. 2*, **81**, 1849 (1985)
- [2] S. S. Brown, J. B. Burkholder, R. K. Talukdar, and A. R. Ravishankara, *J. Phys. Chem. A*, **105**, 1605 (2001)

# Computational Study of Some Hydrogen-Bonded Complexes of Atmospheric Interest

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The inter-conversion of nitrogen oxides and oxy acids on silica surfaces is of major atmospheric importance. As a preliminary step towards rationalising experimental observations, and understanding the mechanisms behind such reactions we have looked at the binding energies of some nitrogen oxides and oxy-acids and the simplest proxies of a silica surface, namely  $\text{SiH}_3\text{OH}$  and  $\text{Si}(\text{OH})_4$  units. The geometries of these molecular dimers were optimised at both HF/6-311+G(d) and B3LYP/6-311+G(d) level. The SCF energies of the species were determined at the HF/6-311++G(3df,2pd) level. The rather large basis set was used to minimise the error due to basis set superposition effects that may be significant when dealing with weakly bound species. Values for  $\Delta H_{298\text{ K}}$  for the following systems have been determined:



The values indicate that nitric acid is by far the most strongly bound species. Future work is planned where we will go beyond the simple cluster treatment presented here and treat the silica surface as a perfect silica surface using periodic quantum mechanical calculations. The adsorption of the nitrogen species may then be treated as a defect on this surface.

# A MATI Spectroscopic Study of n-Butylbenzene Conformers

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Two-colour REMPI and MATI spectra of n-butylbenzene conformers are presented to explore conformational choice in the n-butylbenzene cation. Trans and gauche cation were separately produced by MATI, excitation via the respective S1 origins. Adiabatic ionization potentials of the gauche and trans conformations were determined to be 70154 and 69955 cm<sup>-1</sup> respectively. Analysis of the REMPI and MATI spectra allowed the determination of the energy difference of the S0 (38cm<sup>-1</sup>), S1 (100cm<sup>-1</sup>) and D0 (-161cm<sup>-1</sup>) between gauche and trans conformers.

# The Reactions of $\text{SF}_5\text{CF}_3$ with Ions, Electrons, and Vacuum-UV photons

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Sturges *et al.* [1] have suggested that a new anthropogenic greenhouse gas,  $\text{SF}_5\text{CF}_3$ , recently discovered in the earth's atmosphere has the highest radiative forcing of any gas-phase molecule. Using tunable vacuum-UV (VUV) radiation from a synchrotron and threshold photoelectron – photoion coincidence spectroscopy, we have determined the first dissociative ionisation energy of this molecule (*i.e.*  $\Delta_f\text{H}^0_0$  for  $\text{SF}_5\text{CF}_3 \rightarrow \text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ ), and hence the strength of the  $\text{SF}_5\text{--CF}_3$  bond. Its high value,  $4.06 \pm 0.45$  eV, suggests that this molecule is unlikely to be removed from the earth's atmosphere by UV photolysis in the stratosphere. We are therefore investigating in the laboratory the processes that could remove  $\text{SF}_5\text{CF}_3$  in the mesosphere ; reactions with small cations, electrons, and VUV photodissociation with Lyman- $\alpha$  radiation at 121.6 nm. The total removal rate is  $[\text{SF}_5\text{CF}_3] \cdot (k_{\text{ion}}[\text{ion}] + k_e[\text{e}^-] + \sigma_{121.6} J_{121.6}) \text{ cm}^{-3} \text{ s}^{-1}$ , where  $k_{\text{ion}}$  and  $k_e$  are the bimolecular rate constants for reactions of a cation or electron with  $\text{SF}_5\text{CF}_3$ ,  $\sigma_{121.6}$  and  $J_{121.6}$  are the absorption cross-section of  $\text{SF}_5\text{CF}_3$  and the solar flux at 121.6 nm. We have measured the rate constants for reactions of  $\text{SF}_5\text{CF}_3$  with many cations in a selected ion flow tube at 298 K [3], but the low concentrations of atmospherically-relevant ions in the mesosphere (*e.g.*  $\text{O}_2^+$ ) means that such processes are unlikely to contribute significantly. Electron attachment experiments have been performed in atmospheric pressures of  $\text{N}_2$  and  $\text{Ar}$  buffer gas at 298 K under non-thermal swarm conditions [4]. The rate constant was measured as a function of mean electron energy in the range 0.04–1.90 eV. The estimated thermal attachment rate constant is  $7.7 \pm 0.6 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and more significantly the only observed product,  $\text{SF}_5^-$ , is dissociative. We have also measured the absorption cross-section of  $\text{SF}_5\text{CF}_3$  in the range 50–180 nm, and the cross-section at 121.6 nm is significant,  $1.5 \pm 0.3 \times 10^{-17} \text{ cm}^2$  [5]. It is confirmed that the loss of  $\text{SF}_5\text{CF}_3$  on a molecular basis from the earth's atmosphere is dominated by electron attachment in the mesosphere, yielding  $\text{SF}_5^-$ . The lifetime of  $\text{SF}_5\text{CF}_3$  in the earth's atmosphere, however, is determined by the meterological conditions that globally transfer it from the earth's surface to the mesosphere, and not by the removal processes that occur there. By comparison with data for  $\text{SF}_6$  [6,7], a lifetime of *ca.* 1000 years for  $\text{SF}_5\text{CF}_3$  is determined.

- [1] W. T. Sturges *et al.*, *Science*, (2000) **289**, 611.
- [2] R. Y. L. Chim *et al.*, *J. Phys. Chem. A.*, (2001) **105**, 8403.
- [3] C. Atterbury *et al.*, *Phys. Chem. Chem. Phys.*, (2001) **3**, 1949 and *ibid.* (2002) **4**, 2206.
- [4] R. A. Kennedy and C. A. Mayhew, *Int. J. Mass Spectrom.*, (2001) **206**, i.
- [5] R. Y. L. Chim, R. A. Kennedy and R. P. Tuckett, *Chem. Phys. Letts.*, submitted.
- [6] A. R. Ravishankara *et al.*, *Science*, (1993) **259**, 194.
- [7] R. A. Morris *et al.*, *J. Geophys. Res. D.*, (1995) **100**, 1287.

# Measurement of Rate Constant and Product Branching Ratio in the Reaction ND (a $^1\Delta$ ) + H<sub>2</sub> $\longrightarrow$ Products

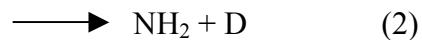
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Kinetic studies have been carried out for the reaction of electronically excited deuterated imidogen radicals with H<sub>2</sub> (ND (a  $^1\Delta$ ) + H<sub>2</sub>  $\longrightarrow$  Products) in the gas-phase using the pulsed laser photolysis-laser-induced fluorescence "pump-and-probe" technique in a flow reactor at room temperature and a total pressure of few Torr. ND (a  $^1\Delta$ ) radicals were generated via the well characterised laser photolysis of DNCO (5 mTorr) at 193 nm which were then allowed to react with H<sub>2</sub> (200-1300 mTorr) excess of argon (total pressure 10 Torr). Argon was used since it thermalises the H atoms very fast but does not quench the ND (a  $^1\Delta$ ) to ND (X  $^3\Sigma$ ). The reaction proceeds via two channels resulting in either H or D atoms as shown below.



Formation of H and D atoms produced in the reaction was monitored using time resolved vacuum ultraviolet laser-induced fluorescence at the Lyman alpha wavelength (H=121.57 and D = 121.53 nm) generated via the four wave mixing technique. Temporal growth of H atoms could be fitted much better than D atoms since there was no H atom background. From the pseudo first order analysis of growth rate of H and D atoms, the rate constant for this reaction was measured to be  $(3.1 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . For the corresponding hydrogenated system, NH (a  $^1\Delta$ ) + H<sub>2</sub>  $\longrightarrow$  Products, we measured a rate constant of  $(3.3 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  which is in reasonable agreement with the value  $(3.76 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  as reported by Tezaki et al. [1]. Within experimental errors, we did not find a significant isotope effect. The product branching ratio was measured to be  $(0.84 \pm 0.06)$  for channel 1.

[1] A Tezaki, S. Okada, K. Yamasaki and H. Matsui, J. Chem. Phys. **98** (1993) 3876.

# The Role of Iron in Sporadic E Layers

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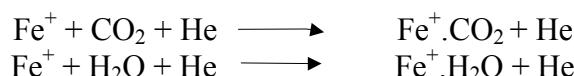
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The major source of metal atoms and ions into the Mesosphere and Lower Thermosphere is the ablation of, on average,  $\sim 120$  tonnes of interplanetary dust every day. The high concentration of atomic oxygen, in this region of the atmosphere, produces a reducing environment which results in the formation of a layer of ionic iron above about  $\sim 90$  km. This layer of  $\text{Fe}^+$  ions is maintained from a layer of neutral Fe atoms (at  $\sim 85\text{-}90$  km) by charge transfer with the ambient ions  $\text{NO}^+$  and  $\text{O}_2^+$ , which are produced by solar photo-ionisation.

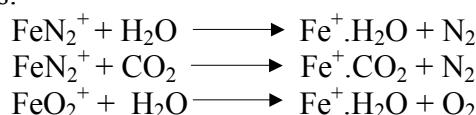
Measurements made with rocket-borne mass spectrometry have shown that the most abundant metallic ion above 90 km is  $\text{Fe}^+$ , with smaller concentrations of  $\text{Mg}^+$  and  $\text{Na}^+$ .  $\text{Fe}^+$  therefore plays a central role in several important plasma-related phenomena.

Sporadic *E* layers are thin layers (1-3 km wide), with high concentrations of metallic ions, that occur in the lower thermosphere between  $\sim 90\text{-}120$  km. They have a significant impact on radio communications, depending on the time of day and the transmission frequency, both by facilitating over-the-horizon HF communication and by obscuring space-to-ground communications.

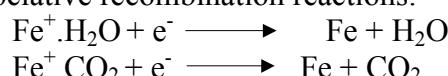
The cycle of reactions concerning  $\text{FeN}_2^+$ ,  $\text{FeO}_2^+$  and  $\text{FeO}^+$  with O, producing  $\text{Fe}^+$ , controls the lifetime of the sporadic *E* layer between 85 – 100 km ( $[\text{O}]/[\text{e}^-] \approx 10^8$  at these heights). As the sporadic *E* layer descends through the atmosphere the ratio  $[\text{CO}_2]/[\text{O}]$  (and to a lesser extent  $[\text{H}_2\text{O}]/[\text{O}]$ ) increases. The iron clusters  $\text{Fe}^+\text{.CO}_2$  and  $\text{Fe}^+\text{.H}_2\text{O}$  can then be produced by either direct reaction with  $\text{Fe}^+$ :



or by the switching reactions:

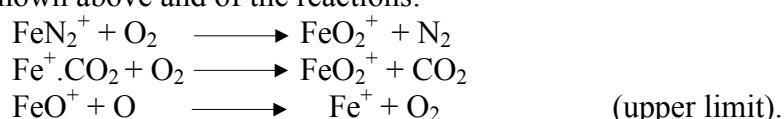


$\text{Fe}^+\text{.CO}_2$  and  $\text{Fe}^+\text{.H}_2\text{O}$  are more resistant to attack by O and are more amenable to attack by  $\text{e}^-$ . The resulting electron dissociative recombination reactions:



produce neutral iron. It is these neutral iron atoms that then appear on Fe LIDAR (Light Detection And Ranging) as a sporadic neutral layer.

We have used the laser ablation of a rotating iron rod in a fast-flow tube to measure the rate constants of the reactions shown above and of the reactions:



# **Ion Imaging Studies of Cl( $^2P_{3/2}$ ) Fragments Arising in the Visible Photolysis of BrCl: Measurement of Orientation, Alignment and Alignment-Free Anisotropy Parameters**

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The photodissociation dynamics of jet-cooled BrCl molecules have been investigated at several different wavelengths in the range 425-485 nm by high resolution velocity map ion imaging methods. Four images of the Cl( $^2P_{3/2}$ ) atomic fragments have been recorded at each photolysis wavelength with the probe laser polarization, respectively, linearly aligned and vertical (*i.e.* perpendicular to the detection axis), right circularly polarized, horizontally linearly polarized (*i.e.* parallel to the detection axis) and left circularly polarized on successive laser shots, thereby ensuring automatic mutual self-normalisation. Appropriate linear combinations of these images allows quantification of the angular momentum alignment of the Cl fragments [*i.e.* the correlation between their recoil velocity (**v**) and their electronic angular momentum (**J**)] in terms of the alignment anisotropy parameters  $s_2$ ,  $\alpha_2$ ,  $\eta_2$  and  $\gamma_2$ , and determination of the ‘alignment-free’ recoil anisotropy parameter,  $\beta_0$ , as a function of parent excitation wavelength. The deduced values of  $\beta_0$  indicate (wavelength dependent) contributions from both parallel and perpendicular parent absorptions in this wavelength range. Such a conclusion accords with approximate deconvolutions of the parent absorption spectrum that are currently available, and with determinations of the orientation parameter  $\gamma_1$  obtained by fitting the difference image obtained when using left and right circularly polarised radiation to probe the ground state Cl atoms arising in the 480.63 nm photodissociation of BrCl when the photolysis laser radiation is polarised linearly at 45° to the detection axis. The deduced values of the alignment parameters provide clear evidence for the importance of non-adiabatic processes in the fragmentation process; they imply both incoherent and coherent contributions to the fragment alignment, and that both simultaneous parallel and perpendicular excitations to the  $B^3\Pi(0^+)$  and  $C^1\Pi(1)$  states, and excitations to the  $\Omega = \pm 1$  components of the C state contribute to the latter.

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